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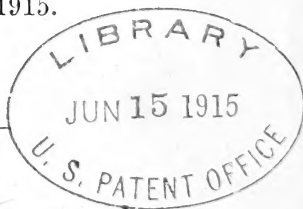
"Nec aranearum sane textus ideo melior quia ex se fila gignunt, nec noster vilior quia ex alienis libamus ut apes." Just. Lips. *Polit.* lib. i. cap. 1. Not.

"Meditationis est perscrutari occulta ; contemplationis est admirari perspicua .... Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem."—*Hugo de S. Victore.*

———" Cur spirent venti, cur terra dehiscat,
Cur mare turgescat, pelago cur tantus amaror,
Cur caput obscura Phœbus ferrugine condat,
Quid toties diros cogat flagrare cometas,
Quid pariat nubes, veniant cur fulmina cœlo,
Quo micet igne Iris, superos quis conciat orbes
Tam vario motu."

J. B. Pinelli ad Mazonium.

ALERE FLAMMAM
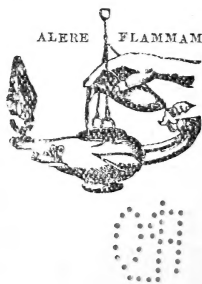
CONTENTS OF VOL. XXIX.

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PLATES.

ERRATA.

Page 104, lines 15 and 16, *for* $\dfrac{w}{a^2}$ *read* $\dfrac{w}{a^2 T_0}$.

Page 105, lines 6, 15, and 20, *for* T *read* T_0.

Page 109, line 1, *for* $\cos^3 \psi$ *read* $\cos^2 \psi$.

Page 114, line 13, *for* $\dfrac{5}{1728}$ *read* $\dfrac{5}{7168}$.

Page 115, in Fig. 3, *for* ξ *read* ζ.

Page 118, line 3, *for* $\left(1 - \dfrac{wl\cos\zeta}{T_2}\right)^t$ *read* $\left(1 - \dfrac{wl\cos\zeta}{T^2}\right)^2$.

Page 122, line 21, after "standard" omit the comma.

Page 127, line 6, *for* "reciprocal" *read* simultaneous.

Page 689, line 8, *for* "$12 - \rho'/\rho$" *read* "$1 - 2\rho'/\rho$."

Page 698, line 17, *for* "$\frac{1}{2}\kappa =$" *read* "$\kappa = \frac{1}{2}$."

I. *On the most Effective Adjustment of an Induction-coil.*
   By E. TAYLOR JONES, *D.Sc., Professor of Physics in the*
   University College of North Wales, Bangor *.

[Plate I.]

IN a recent paper † it was shown that the secondary
potential and spark-length developed by an induction-
coil, when a given current is interrupted in the primary
circuit, are greatest under the following conditions :—

> (1) The ratio n_2/n_1 of the two frequencies of elec-
> trical oscillation of the system has one of the values
> 3, 7, 11, ... ;
> (2) $L_1 C_1 = (1 - k^2) L_2 C_2$ ‡.

The first is the condition that maxima of the two potential
waves in the secondary circuit should occur simultaneously,
the second that the sum of the amplitudes of the two waves
should be a maximum for a given value of k.

It was further stated that the most effective of the ratios
specified in (1) is $n_2/n_1 = 3$, and that in this case the
conditions are satisfied by the adjustment $k = \cdot756$,
$L_1 C_1 = \cdot429\ L_2 C_2$.

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* Communicated by the Author.
† Phil. Mag. xxvii. pp. 580–586, April 1914.
‡ L_1, L_2 are the self-inductances, C_1, C_2 the capacities, and k is the
coupling coefficient of the primary and secondary circuits.

The physical meaning of the above results may be further considered in the light of what goes on in the *primary* circuit after the interruption of the current. An expression for the potential-difference V_1 of the plates of the primary condenser, at any time t after the interruption of the current i_0, has been given by Dibbern [*]. If the resistances of the circuits are neglected, Dibbern's expression becomes

$$V_1 = \frac{2\pi i_0 n_1 n_2{}^2}{C_1(n_2{}^2 - n_1{}^2)}\left(\frac{1}{4\pi^2 n_2{}^2} - L_1 C_1\right)\sin 2\pi n_1 t$$
$$- \frac{2\pi i_0 n_1{}^2 n_2}{C_1(n_2{}^2 - n_1{}^2)}\left(\frac{1}{4\pi^2 n_1{}^2} - L_1 C_1\right)\sin 2\pi n_2 t.$$

If n_2/n_1 has one of the values 3, 7, 11, ..., then at the time $t = 1/4n_1$, $\sin 2\pi n_1 t = 1$, and $\sin 2\pi n_2 t = -1$. Consequently the value of V_1 becomes at this instant

$$\frac{i_0}{2\pi C_1} \cdot \frac{1}{n_2 - n_1} - 2\pi i_0 L_1 \cdot \frac{n_1 n_2}{n_2 - n_1}.$$

This may be expressed in terms of the ratio $L_2 C_2/L_1 C_1$. Calling this m, and writing a for $\dfrac{1}{8\pi^2 L_2 C_2(1 - k^2)}$, we have

$$n_1 n_2 = 2a\sqrt{m(1 - k^2)},$$
$$n_2 - n_1 = \sqrt{2a(m + 1) - 4a\sqrt{m(1 - k^2)}} \; [†].$$

Hence $$V_1 = \frac{i_0\{1 - 8\pi^2 L_1 C_1 a\sqrt{m(1 - k^2)}\}}{2\pi C_1\sqrt{2a(m + 1) - 4a\sqrt{m(1 - k^2)}}}.$$

Inserting the value of a and condition (2), *i. e.* $m = \dfrac{1}{1 - k^2}$, we find that this expression vanishes.

It appears, therefore, that if conditions (1) and (2) are satisfied, the amplitudes of the two potential waves in the primary circuit are equal, and that at the instant in question the potentials are at their maxima, but in opposite phase. The primary condenser is therefore uncharged, while at the same moment the secondary potential is at its maximum [‡], the two waves in the secondary circuit being then at their maxima and in the *same* phase. Further, since $dV_1/dt = 0$, and $dV_2/dt = 0$, there is no current in either circuit. The whole of the energy therefore exists at this moment in the

* E. Dibbern, *Ann. d. Physik*, xl. 4, p. 938 (1913); Inaug. Diss., Kiel.
  † *L. c.* p. 581.   ‡ *L. c.* p. 581.

electrostatic form in the secondary circuit, and the secondary potential must in these circumstances have its greatest possible value for a given initial energy-supply $\frac{1}{2}L_1 i_0^2$.

It was shown in the previous paper to which reference has been made * that the value of this maximum secondary potential, still on the assumption that the resistances are negligible, is

$$V_{2m} = i_0 \cdot \frac{L_{21}}{\sqrt{L_2 C_2}} \cdot \frac{1}{k} \quad \ldots \quad (3\,a)$$

$$= i_0 \sqrt{\frac{L_{21}}{L_{12}}} \cdot \sqrt{\frac{L_1}{C_2}} \cdot \quad \ldots \quad (3\,b)$$

The energy equation is therefore

$$\tfrac{1}{2}L_1 i_0^2 = \tfrac{1}{2}C_2 V_{2m}^2 \cdot \frac{L_{12}}{L_{21}}.$$

The factor L_{12}/L_{21} arises from the manner in which the capacity C_2 of the secondary circuit is defined. It is the charge on one-half of the secondary coil (and the bodies connected to its terminal), divided by the difference of potential of the terminals. The charge on this portion of the secondary circuit is $C_2 V_{2m}$, but as some of this charge is at a lower potential than that of the terminals, the energy must be less than $\frac{1}{2}C_2 V_{2m}^2$. The correcting factor is L_{12}/L_{21}.

There are many values of k and $L_1 C_1/L_2 C_2$ which satisfy the above conditions. The first four, probably the only ones having any practical importance, are given in Table I.

TABLE I.

n_2/n_1.	k.	$\dfrac{L_1 C_1}{L_2 C_2} = 1 - k^2$.
3	·756	·429
7	·914	·164
11	·950	·098
15	·965	·070

If we define the efficiency of an induction-coil as the ratio of the maximum electrostatic energy in the secondary to the electrokinetic energy in the primary circuit just before the interruption of the current (*i. e.*, $\frac{1}{2}L_1 i_0^2$), then the efficiency

* *L. c.* pp. 581, 584.

is unity in each of the adjustments specified in Table I. if the resistances of the circuits are negligible. But it is easy to see that of these adjustments the first (*i. e.*, $n_2/n_1 = 3$, $L_1 C_1 = \cdot 429\, L_2 C_2$) is the one which gives the longest spark *for a given primary current.* For let us suppose that an induction-coil is so constructed, and the primary condenser so chosen, that $k = \cdot 914$ and $L_1 C_1 = \cdot 164\, L_2 C_2$. This is the second adjustment of Table I., and it allows the whole of the primary energy $\frac{1}{2} L_1 i_0{}^2$ to be converted at a certain moment after the interruption into electrostatic energy in the secondary circuit. Now by inserting coils of suitable self-inductance, say l_1, in the primary circuit (coils which do not act inductively on the induction-coil) we can reduce the coupling coefficient to $\cdot 756$; and if the primary condenser is chosen so that $(L_1 + l_1) C_1 = \cdot 429\, L_2 C_2$, we then have the first adjustment, with $n_2/n_1 = 3$. The system has again unit efficiency, but the maximum electrostatic energy in the secondary is now $\frac{1}{2}(L_1 + l_1) i_0{}^2$, and is greater than the former value in the ratio of $L_1 + l_1$ to L_1. The capacity C_2 of the secondary coil being unaltered, the secondary potential is increased in the ratio $\sqrt{L_1 + l_1}$ to $\sqrt{L_1}$. The $3/1$ adjustment is thus more effective (though not more efficient) than the others because it allows a greater quantity of initial energy to be converted into electrostatic energy in the secondary circuit, in which therefore the charge and potential developed are greater than in the other cases.

There are other ways in which the coupling coefficient could be reduced (*e. g.*, from $\cdot 914$ to $\cdot 756$), but none of them are so effective as the plan of introducing external inductance into the primary circuit. For instance [*], external inductance may be introduced in the *secondary* circuit. This increases C_2, and to some extent L_{12}, without altering L_1 and L_{21}, and therefore, by (3 *b*), lowers the secondary potential. Again, k may be reduced by removing a part of the iron core. This diminishes L_1 without causing any increase in L_{21}/L_{12}, or any change in C_2, and therefore, by (3 *b*), reduces V_{2m}. The reduction of the coupling may also be effected by withdrawing the primary coil with the core to a suitable distance along the axis of the secondary. This process reduces L_{12}, L_{21}, and L_2, without changing L_1, and should cause no change in the secondary potential except such as may be due to a slight diminution of C_2 or of the ratio L_{21}/L_{12}.

It should be clearly understood that these reductions of the coupling are supposed to bring the system from

[*] In each of these supposed modifications the primary capacity is to be adjusted so that $L_1 C_1 = (1 - k^2) L_2 C_2$.

one state of unit efficiency to another, *e. g.* from the second to the first adjustment of Table I., for it is only in these states that equations (3 *a*), (3 *b*) hold. If, on the other hand, *k* lies between two of the unit-efficiency values, the spark-length for a given current may be increased by withdrawing the primary coil and core to a suitable distance along the axis of the secondary. For example, the coil with which I have experimented has a coupling coefficient of ·876, and the longest spark occurs when the primary capacity is about ·06 microfarad *. A marked increase is, however, produced in the spark-length by withdrawing the primary coil and core to a distance of 36·5 cm. from its nearly symmetrical position in the secondary, and increasing the capacity to ·15 microfarad.

We may conclude that any induction-coil in which the coupling is greater than ·756 can be improved in spark-length by connecting external series inductance in the primary circuit so as to reduce the coupling to this value. An induction-coil should not be constructed so that the coupling is less than ·756, for there is no convenient way of increasing the coupling to this value. Nor should the coupling coefficient of the primary and secondary *coils* have precisely this value, though if no external coils are used this is the best arrangement. Better effects are obtained by coupling the coils more closely than this, and adding series inductance to the primary circuit so as to reduce *k* to this value. The ratio L_1/C_2 is thereby increased, and it is upon this quantity, when the adjustments (1) and (2) are effected, that the maximum secondary potential for a given primary current chiefly depends.

In fig. 1 (A) are shown curves representing the two potential waves in the primary circuit of an induction-coil in which the above adjustment has been effected, and in which the damping of the oscillations is negligible. The amplitude of each wave is taken as 5000 volts, and the periods are ·0024 sec. and ·0008 sec. These values are chosen so as to correspond approximately (for $i_0 = 10$ amperes) with those found in an actual case, as described below. Fig. 1 (B) shows the result of superposing the two curves of (A). The equation to curve (B), the ordinate of which represents the potential of the primary condenser *t* seconds after the interruption, is

$$V_1 = -5000 \sin 150,000\, t - 5000 \sin 450,000\, t,$$

the angles being given in degrees.

* It was explained in the previous paper (*l. c.* pp. 584, 585) how the most effective primary capacity in any such case can be calculated.

Fig. 1.

Primary potential.
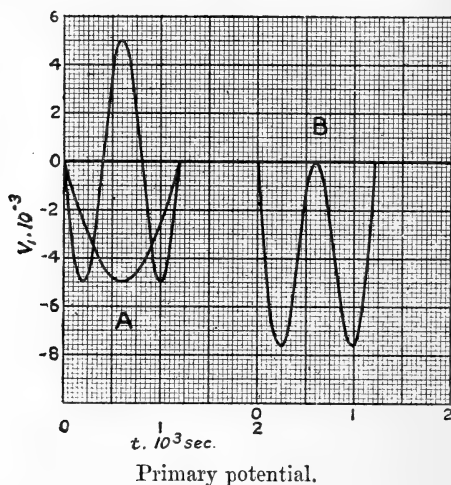
The curves in fig. 1 cover one half-period of the longer wave ; their continuation in the second half-period is merely a repetition with the ordinates reversed in sign.

Fig. 2.

Secondary potential.
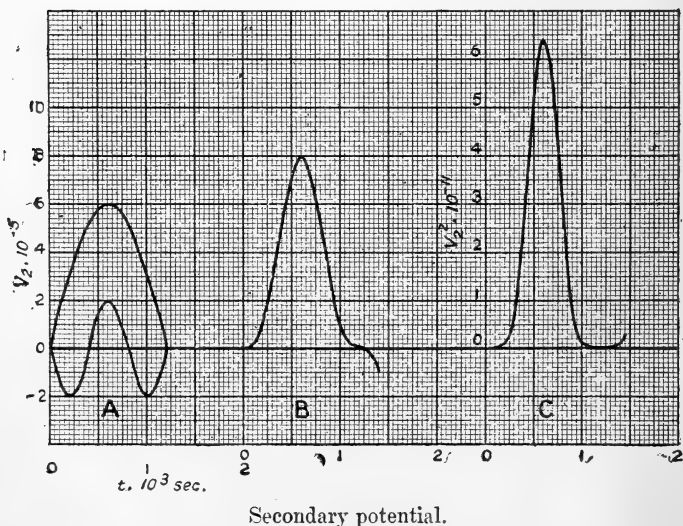
Fig. 2 (A) shows the corresponding potential waves in the secondary circuit ; fig. 2 (B) the effect of their superposition. The amplitudes here are taken as 600,000 and 200,000 volts

respectively. It will be seen that the two positive maxima coincide at ·0006 sec. after the interruption, giving the maximum potential of 800,000 volts at the secondary terminals. At this moment the potential of the primary condenser is zero. Fig. 2 (C) shows (for comparison with the oscillograph curves described below) the curve obtained by squaring the ordinates of fig. 2 (B).

The above theoretical conclusions apply strictly only to the case of an ideal induction-coil, in which the resistances of the circuits and other causes of damping of the oscillations are negligible. Some applications of the theory were, however, given, in the former paper referred to *, in which it was shown that the results of the theory agree closely with experiment in so far as they concern the *conditions* under which the greatest spark-length is given by an induction-coil. The *value* of the secondary ·potential is of course greatly modified by the damping.

Another experiment will now be described, from the results of which some further information may be gathered as to the working of an induction-coil when in its most effective adjustment.

The coil experimented upon was the one employed in the previous experiments, viz.: an 18-inch coil in which the coefficient of coupling of the primary and secondary coils (the secondary terminals being connected to the oscillograph and to a variable spark-gap) is ·876. The primary circuit was fed by a number of storage-cells, and included an amperemeter, a rheostat, and a slow interruptor which broke the current about once per second. The condenser was connected directly across the interruptor.

The experiment consisted in increasing the self-inductance of the primary circuit by the addition of air-core coils, and varying the capacity of the condenser, until the longest spark was produced by a given primary current. The curve of secondary potential was then photographed, and the constants of the circuits determined. The best effect was found to be obtained with four extra coils in the primary circuit, and with a condenser of ·2 microfarad capacity. It was not very easy to decide with great exactness upon the best self-inductance and capacity, owing to the fact that the spark-length varies slowly with these quantities in the neighbourhood of the maximum. A difference of ·025 mfd. either way in C_1 caused no appreciable change in the spark-length. From the practical point of view this slow variation near the maximum is in itself no disadvantage, since very exact

adjustment is not necessary in order to produce a spark-length practically equal to the maximum.

The constants of the circuits were measured by methods which were fully described in the previous paper, and found to be as follows :—

$$\frac{1}{L_1 C_1} = 19{\cdot}57 \,.\, 10^6 \text{ c.g.s.,}$$

$$\frac{1}{L_2 C_2} = 8{\cdot}763 \,.\, 10^6 \quad \text{,,}$$

$$k = {\cdot}748,$$

$$L_{21} = 20{\cdot}4 \text{ henries,}$$

$$\frac{R_1}{L_1} = 680,$$

$$\frac{R_2}{L_2} = 825.$$

R_0, the resistance of the primary circuit for steady currents, was 8 ohms.

Hence

$$\theta_1 = \tfrac{1}{2} R_1 C_1 = 1{\cdot}738 \,.\, 10^{-5} \text{ c.g.s.}$$
$$\theta_2 = \tfrac{1}{2} R_2 C_2 = 4{\cdot}709 \,.\, 10^{-5} \quad \text{,,}$$
$$\theta_0 = \tfrac{1}{2} R_0 C_1 = \qquad 8 \,.\, 10^{-7} \quad \text{,,}$$

The quantities R_1/L_1, R_2/L_2, were determined from the decay factors of the circuits when oscillating separately. The effective resistances R_1, R_2, are much greater than the steady-current values ; they depend also upon losses due to leakage, hysteresis, and absorption. A considerable part of R_2 is probably due to leakage through the electrometer. The decay factors are not constant ; the values of R_1/L_1, R_2/L_2 given above prevail during oscillations of fairly large amplitude in the primary and secondary circuits respectively.

The calculated frequencies are :

$$n_1 = 413{\cdot}9,$$
$$n_2 = 1208,$$

giving
$$n_2/n_1 = 2{\cdot}919.$$

Also
$$L_1 C_1 / L_2 C_2 = {\cdot}448,$$

while
$$1 - k^2 = {\cdot}440.$$

The differences between these values and those of the ideal case ($n_2/n_1 = 3$, $k = {\cdot}756$, $L_1 C_1 / L_2 C_2 = {\cdot}429$) are within the limits of experimental error, and may be due to the above-mentioned difficulty of adjusting L_1 and C_1 accurately

to give the best effect. If L_1 and C_1 were reduced, by amounts which would cause no appreciable change in the spark-length, the differences would disappear.

From the above data the secondary potential can now be calculated [*], and the result, expressed in volts for $i_0 = 10$ amperes, is

$$V_2 = 601300 \cdot e^{-266\,t} \sin(149000\,t - 1.95)°$$
$$- 206900 \cdot e^{-1440t} \sin(435000\,t - 5.7)°.$$

From this expression values of V_2, the difference of potential at the secondary terminals t seconds after the interruption of the primary current, were calculated for

Fig. 3.
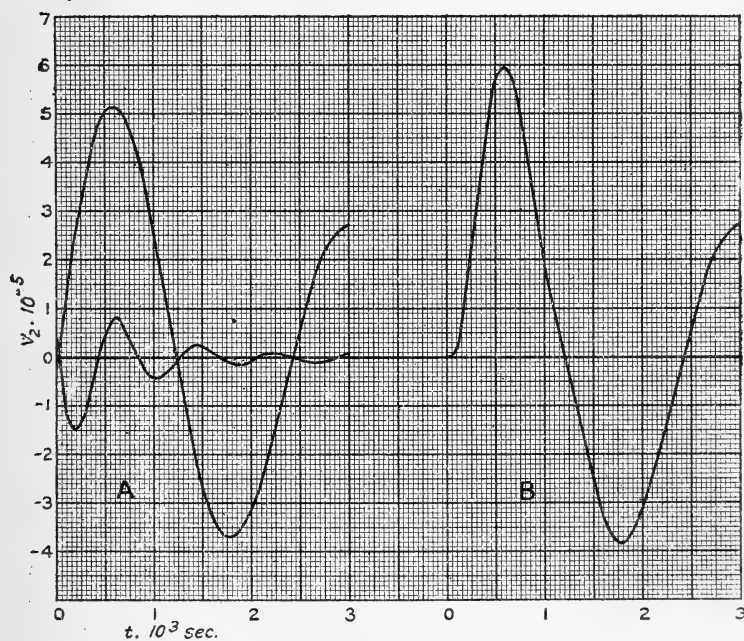
Secondary potential.

various values of t up to ·003 second, a time covering rather more than one whole period of the longer wave. The results are exhibited in fig. 3, in which (A) shows the two oscillations

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[*] The general expression for V_2 is given in the previous paper, *l. c.* pp. 565, 574. The statement in the footnote on p. 574 requires correction. When the condenser is connected directly across the interruptor, so that the battery (e.m.f. E) is included in the primary oscillating circuit, we have initially $V_1 = 0$, but finally $V_1 = -E$. The results as given on pp. 574, 575, apply to this case provided V_1 is taken as E + the potential-difference of the primary condenser.

of the secondary circuit separately, and (B) the result of their superposition. It will be seen that two positive maxima in the oscillations agree at about $t = \cdot0006$ sec., giving rise to the maximum secondary potential (596900 volts) at this time. Fig. 4 shows the square of the secondary

Fig. 4.
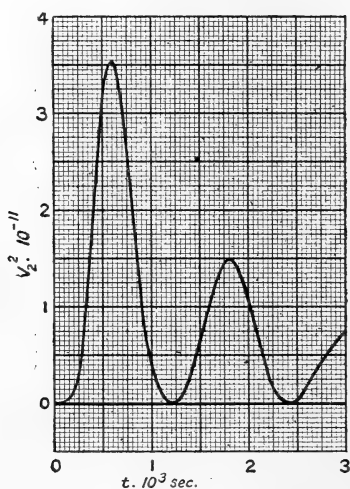
Square of secondary potential.

potential plotted against the time. This curve shows clearly the peaked maxima and the flattened zeroes which are characteristic of the 3/1 ratio.

In Plate I. figs. 6 and 7 are shown photographic records of the secondary potential wave obtained with the oscillograph. In these curves the ordinates are proportional to the square of the secondary potential, owing to the idiostatic connexion of the instrument, and these curves are therefore directly comparable with fig. 4. The currents interrupted when these photographs were taken were 1·5 and 2·0 amperes respectively *. It will be seen that the greatest ordinates of the curves are proportional to the squares of the currents. In period †, rate of decay, and form the calculated curve of fig. 4 agrees well with the photographs. The photographic curves are perhaps rather more

* The greatest spark-length for 2 amperes, between spark-balls 2 cm. in diameter, was 18·2 cm. The external inductance being removed, and the primary coil being still in its symmetrical position within the secondary, the greatest spark-length at 2 amperes ($C_1 = 0·6$ mfd.) was 12·8 cm. No sparks passed when the photographs shown were taken.

† The time curve shown on the photographs has a period of 1/768 sec.

peaked at the summits, and more flattened at the zeroes, than the calculated curve, which indicates that the calculated damping factor of the shorter wave is rather too great in comparison with that of the slower oscillation. This may possibly be due to the existence of an appreciable difference (arising from various causes) between the values of the effective resistances of the circuits when oscillating separately, and their values when the circuits are oscillating as a coupled system.

Turning now to the primary circuit, Dibbern's formula allows the potential wave in the primary condenser to be calculated *. Using the values given above for the constants of the circuits, and taking i_0, the primary current interrupted, as 10 amperes, Dibbern's expression becomes in the present case

$$V_1\dagger = -5020\,e^{-266\,t}\sin{(149000\,t + 8 \cdot 02)^\circ}$$
$$- 4940\,e^{-1440\,t}\sin{(435000\,t - 9 \cdot 07)^\circ}, \quad . \quad . \quad (4)$$

where V_1 is the primary potential in volts.

The amplitudes of the two oscillations in the primary circuit are thus nearly equal, as required by condition (2).

The two oscillations represented by (4) are shown in fig. 5 (A), the result of their superposition in fig. 5 (B). It will be seen that the negative potential‡ of the primary condenser reaches a maximum of 6800 volts at about ·00025 sec., and a minimum of 2250 volts at about ·00065 sec. after the interruption. Thus, at the moment at which the secondary potential reaches its greatest value the primary condenser, instead of being uncharged as would be the case in an ideal induction-coil, is still charged to about 2250 volts, and this is due almost entirely to the difference in the damping factors of the two oscillations.

The effective resistances of the circuits therefore act in two ways in reducing the efficiency of the arrangement. First, they give rise to dissipation of energy and consequent decay of the amplitudes of both oscillations. Second, owing to the difference between the damping factors of the two oscillations, there is some energy stored in the primary condenser at the moment when the secondary potential is at its maximum.

* The existence of the two oscillations in the primary circuit after the interruption is well shown by a current oscillogram taken by Wertheim-Salomonson, *Physik. Zeitschr.* xi. p. 539, fig. 1 (1910).

† As explained in the footnote on p. 9 above, V_1 here means $E +$ the potential of the condenser. E is here 80 volts.

‡ The potential of the primary condenser is taken negative when it opposes the battery E.M.F.

The efficiency is easily calculated in the present case. The maximum secondary potential, for $i_0 = 10$ amperes, is 596900 volts. If the resistances were negligible, and if the system

Fig. 5.
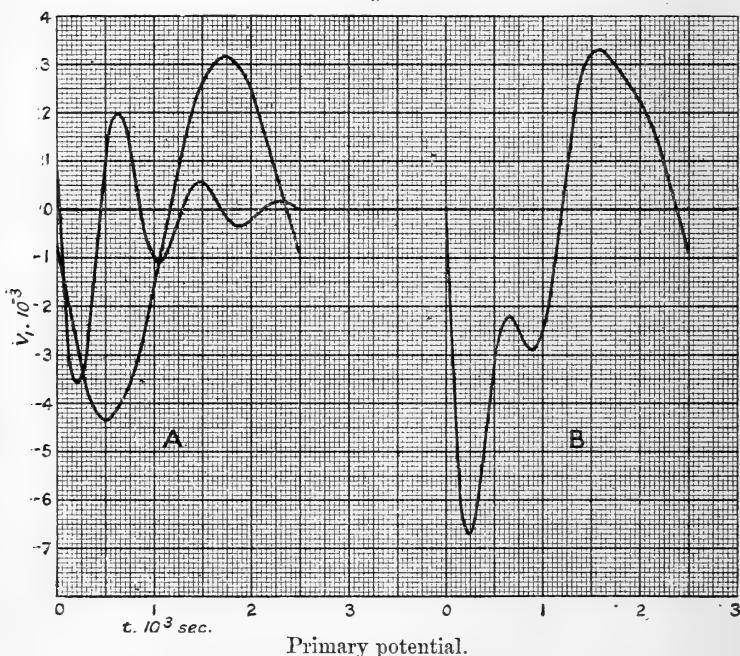
Primary potential.

were exactly in the first unit-efficiency adjustment, the maximum secondary potential would be, by (3a), 798700 volts. Consequently the efficiency is $\left(\dfrac{5969}{7987}\right)^2 = \cdot 559$.

The energy originally in the system is $\frac{1}{2} L_1 i_0^2$, *i. e.* since L_1 is about $\cdot 255$ henry, $12\cdot 75$ joules. The maximum electrostatic energy in the secondary circuit is therefore $\cdot 559 \times 12\cdot 75$, or about $7\cdot 1$ joules. The energy then stored in the primary condenser (capacity $\cdot 2$ mfd.) is $\frac{1}{2} \cdot \cdot 2 \cdot 2250^2 \cdot 10$ ergs, or about $\cdot 5$ joule.

Consequently of the original $12\cdot 75$ joules rather over 5 are dissipated, half a joule is stored in the primary condenser, and the remaining 7 joules are available to provide for the secondary discharge at the moment of maximum potential.

The charge then on the secondary is $C_2 V_2$ and may be calculated when the capacity C_2 is known. If we knew the value of the ratio L_{21}/L_{12} the capacity could be at once

determined from the known values of k^2, L_1, L_{21}, and L_2C_2, since

$$C_2 = \frac{L_{21}}{L_{12}} \cdot \frac{L_1}{L_{21}{}^2} \cdot k^2 \cdot L_2C_2. \quad \ldots \quad (5)$$

With regard to the ratio L_{21}/L_{12}, this differs from unity because the current in the secondary coil during the oscillations is not uniformly distributed, but is greatest at the central winding and nearly zero at the ends. If all the windings of the secondary had equal inductive effects on the primary, when reckoned per unit current, and if the current in a turn of the secondary at a distance z from the central winding were proportional to $\cos\dfrac{\pi z}{h}$, where h is the length of the secondary coil, it is easily seen that L_{21}/L_{12} would be equal to $\pi/2$. In the actual case, however, the inductive effect of the secondary windings (per unit current) diminishes from the centre towards each end. This was tested by ballistic galvanometer experiments in which the mutual inductance of the primary and a single turn of wire, wound on the secondary (or primary) in various positions, was compared with its value for the central position. From the results of these measurements it was found that this mutual inductance could be represented approximately by the expression $a - bz^2 - cz^4$ *. Consequently L_{12} is proportional to

$$\int_{-h/2}^{+h/2} (a - bz^2 - cz^4) \cos\frac{\pi z}{h}\,dz,$$

while L_{21} is proportional to

$$\int_{-h/2}^{+h/2} (a - bz^2 - cz^4)\,dz,$$

since the current in the primary coil is uniformly distributed. The value of L_{21}/L_{12} is thereby reduced from $\pi/2$, and becomes in the present case $\cdot 95\,\pi/2$.

Another correction is necessary if, as in the present experiments, the secondary terminals are connected to a capacity which is not negligible in comparison with that of the coil. In this case the secondary current is not quite zero at the ends of the coil, but should be represented as proportional to $\cos\dfrac{\pi z}{h'}$, where h' is greater than h. The value

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* The dimensions of the coils are :—primary, length 90 cm., mean diameter 6·9 cm. ; secondary, length (between the terminals) 51 cm., diameter (outside) 24 cm.

of h' may be estimated if we know the ratio of the external capacity C_e to the total capacity C_2. If C_e is small in comparison with C_2 the approximate value of the latter (obtained from equation (5) by neglecting the present correction) may be used here. If the current in the secondary windings varies as $\cos \dfrac{\pi z}{h'}$, the charge per unit length will be proportional to $\sin \dfrac{\pi z}{h'}$. Hence the ratio of C to C_2 is equal to the ratio of

$$\int_{h/2}^{h'/2} \sin \frac{\pi z}{h'} \cdot dz \qquad \text{to} \qquad \int_0^{h'/2} \sin \frac{\pi z}{h'} dz,$$

i. e. $\dfrac{C_e}{C_2} = \cos \dfrac{\pi h}{2h'}.$

This determines h'/h, and we then have

$$\frac{L_{12}}{L_{21}} = \frac{1}{h} \int_{-h/2}^{+h/2} \cos \frac{\pi z}{h'} dz$$

$$= \frac{2}{\pi} \cdot \frac{h'}{h} \cdot \sin \frac{\pi h}{2h'}.$$

In the present experiments C_e is the capacity of the electrometer and the spark-gap terminals, and this is about one-sixth of the total secondary capacity C_2, the value of which is already known approximately. Hence $\cos \dfrac{\pi h}{2h'} = \dfrac{1}{6}$, and $\dfrac{h'}{h} = 1\cdot12$, from which $\dfrac{L_{12}}{L_{21}} = 1\cdot10 \cdot \dfrac{2}{\pi}$. The effect of this correction is therefore further to reduce L_{21}/L_{12} by about 10 per cent.

Taking both corrections into account we have approximately

$$L_{21}/L_{12} = \cdot85\pi/2 = 1\cdot335,$$

from which by (5)

$$C_2 = \cdot000052 \text{ microfarad.}$$

The charge of the secondary circuit at the moment of maximum potential is therefore $5\cdot2 \times 5\cdot969 \times 10^{-7}$ c.g.s., or $31 \cdot 10^{-6}$ coulomb. If the whole of this charge escaped from the terminals, in the form of a spark or other discharge, the discharge current would be, at n interruptions per second, nC_2V_2. Further experiments are, however, required in order to decide whether this complete discharge takes place, or whether some of the electricity does not return through the secondary coil and continue to oscillate in it.

The conditions for maximum potential are the same when a rapid interruptor is employed as for the slow break used in the above experiments. They also hold whether the primary current is supplied by a small storage-battery, a 100-volt battery, or the 200-volt mains. Plate I. fig. 8 shows the course of the secondary potential at two successive " breaks " effected by a motor mercury interruptor. The effect of the small potential at the " make " is also noticeable. On this occasion the 100-volt battery was used to supply the primary current, the total (steady-current) resistance in the primary circuit being 11 ohms. The greatest spark-length was 18·4 cm., and the mean primary current, as indicated by an amperemeter in the primary circuit, was ·3 ampere. The current immediately before interruption would, however, be over 2 amperes.

Bangor, November 1914.

II. *On Motion in a Periodic Field of Force.*
By C. V. RAMAN, *M.A.*[*]

[Plate II.]

Vibrations maintained by a Periodic Field of Force.

THE experimental study of the motion of a dynamical system in a periodic field of force leads to results of quite exceptional interest. One aspect of the problem, *i. e.* the oscillatory motion of the system about a position of equilibrium in the field, has some affinities to the case of vibrations maintained by a variable spring which I have dealt with in my previously published work, but the two classes of investigations lead to results which differ from one another, yet are related in a most remarkable way. By experimenting on stretched strings subjected to a variable tension, I showed that a normal variation of spring will enable the oscillations of the system to be maintained, when the frequency of these oscillations is sufficiently nearly equal to $\frac{1}{2}$ of, or $\frac{2}{2}$ times, or $\frac{3}{2}$ times, or $\frac{4}{2}$ times, &c. the frequency of variation of the spring, these ratios forming an ascending series [†]. By experiments on the vibrations of a body about a position of equilibrium in a periodic field of force (to be described below), I have shown that the frequency of the oscillations maintained may be equal to, or half of, or one-third, or one-fourth, &c. of the frequency of the field; in other words, it

[*] Communicated by the Author.
[†] See Phil. Mag. Oct. 1912, " The Maintenance of Forced Oscillations of a New Type."

may be any one of a descending series of sub-multiples of the frequency of the field. It appears, in fact, that we have here an entirely new class of resonance-vibrations. It will be noticed that if the two series referred to above are both written in the same order of descending magnitudes of frequency, thus,

$$\frac{6}{2}, \frac{5}{2}, \frac{4}{2}, \frac{3}{2}, \frac{2}{2}, \frac{1}{2},$$

$$\frac{1}{1}, \frac{1}{2}, \frac{1}{3}, \frac{1}{4}, \frac{1}{5}, \frac{1}{6},$$

the last two terms of the first series, and the first two of the second series coincide, and these two are to some extent typical of the rest. For, as I have shown in a previous publication *, the 1st, the 3rd, the 5th, and the odd types generally in the first series bear a family resemblance to each other, giving symmetrical vibration curves. The 2nd, the 4th, and the other even types similarly resemble each other in giving markedly *asymmetrical* vibration curves. Since the first term in the ascending series is the 2nd in the descending series, we may expect that the 2nd, 4th, 6th, &c. in the latter would give analogous types of motion, and that similarly the 1st, 3rd, 5th, &c. would show resemblances amongst each other. These points will be dealt with more fully as we proceed.

The vibrations studied which form the subject of this section were those of the armature-wheel of a synchronous motor of the attracted-iron type, about a position of equilibrium in the magnetic field produced by an intermittent current circulating in the coils of an electromagnet. The phonic wheel or synchronous motor devised by La Cour and Lord Rayleigh is, as is well known, of great service in acoustical investigations. In my own work on vibrations and their maintenance, it has been of considerable assistance. Apart, however, from the various uses of the instrument in different branches of Physics and in Applied Electricity, it possesses much intrinsic interest of its own as an excellent illustration of the dynamics of a system moving in a periodic field of force, and the present paper deals almost entirely with experiments carried out by its aid and with its applications to the study of vibrations.

The instrument used by me was supplied by Messrs. Pye & Co., of Cambridge, and has given entire satisfaction. The motor consists of a wheel of soft iron mounted on an axis with ball-bearings between the two poles of an electromagnet placed diametrically with respect to it. The wheel has thirty

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* See Physical Review, Dec. 1912.

teeth, and when a direct current is passed through the electro-magnet, sets itself rigidly at rest with a pair of teeth at the ends of a diameter opposite the two poles of the electro-magnet. The equilibrium under such conditions is of course thoroughly stable, and, in fact, the wheel possesses a fairly high frequency of free angular oscillation for displacements from this position of rest, and any motion set up by such displacement rapidly dies out, apparently on account of Foucault currents induced in the iron by the motion. This, in general, is also true when an intermittent current supplied by a fork-interrupter is used to excite the electromagnet, except however in certain cases, when it is observed that the equilibrium becomes unstable of its own accord and the wheel settles down into a state of steady vigorous vibration about the line of equilibrium : or that an oscillation of sufficient amplitude once started maintains itself for an indefinitely long period.

An optical method can be conveniently used to study the frequency and the phase of the oscillations of the armature-wheel maintained in the manner described above. A narrow pencil of light is used, which first suffers reflexion at the surface of a small mirror attached normally to one of the prongs of the fork-interrupter furnishing the intermittent current, and then falls upon a second similar mirror attached to the axle of the armature-wheel parallel to its axis of rotation. The apparatus is so arranged that the angular deflexions produced by the oscillations of the fork and the wheel are at right angles to each other, and the pencil of light which falls upon a distant screen, or which is focussed on the ground-glass of the photographic camera, is seen to describe a Lissajous figure from which the frequency, and the phase-relations between the oscillations of the fork-interrupter and of the armature-wheel, can be readily ascertained. It is then observed that the period of the vibration of the armature-wheel is equal to, or twice, or thrice, or four times, &c. the period of the fork : in other words, the frequency is equal to or $\frac{1}{2}$ of or $\frac{1}{3}$ or $\frac{1}{4}$ or $\frac{1}{5}$ or $\frac{1}{6}$ that of the fork.

In making the experiments, the motor-wheel is relieved of the large stroboscopic disk that is usually mounted upon it, and in working down the series, the adjustment of frequency is secured by suitably loading the wheel. The *fine* adjust-ment for resonance is effected by altering the current passing through the interrupter with the aid of a rheostat, and if necessary by regulating the contact-maker on the fork. Any oscillation of the wheel, when started, dies away except in the cases referred to above ; in other words, no frequencies

intermediate between those of the series are maintained. In obtaining the 1st case, in which the oscillations of the wheel and the fork are in unison, it is generally found necessary to increase the " spring " of the wheel by passing a steady direct current through the electromagnet of the motor from a cell connected in parallel, in addition to the intermittent current flowing in the same direction from the interrupter circuit.

It is found that the Lissajous figures for the 1st, 3rd, and 5th cases are distinctly asymmetrical in character, the 3rd being markedly so. The 2nd, 4th, and 6th types are quite symmetrical. This, it will be remembered, was what was anticipated above, and in fact the 1st, 3rd, and 5th types differ rather markedly in their behaviour from the 2nd, 4th, and 6th types. These latter are maintained with the greatest ease, while the former, particularly the 5th, are not altogether so readily maintained. In fact it is found advantageous, in order to maintain the 5th type steadily, to load the wheel somewhat unsymmetrically and to put it a little out of level, in order to allow the oscillations to take place about an axis slightly displaced from the line joining the poles of the electromagnet.

It is noticed also that the lower frequencies of vibration have much larger amplitudes. This, I would attribute principally to the greatly reduced damping at the lower frequencies owing to the slower motion, the larger masses, and the weaker magnetic fields employed.

We are now in a position to consider the mathematical theory of this class of maintained vibrations. To test the correctness of my theoretical work, I have prepared a series of photographs of the simultaneous vibration-curves of the fork and of the armature-wheel, which are reproduced as figs. 1 to 6, Pl. II. These curves were obtained by the usual method of recording the vibrations optically on a moving photographic plate, it being so arranged that the directions of movement of the two representative spots of light on the plate lie in the same straight line. The upper curve in each case shows the maintained vibration of the armature-wheel. The lower represents that of the fork-interrupter. The frequency of the former, it will be seen, is $\frac{1}{1}$ or $\frac{1}{2}$ or $\frac{1}{3}$ or $\frac{1}{4}$ or $\frac{1}{5}$ or $\frac{1}{6} \times$ that of the latter. The precise features of the vibration-curve noticed in each case will be referred to below, in connexion with the mathematical discussion.

The equation of motion of a system with one degree of freedom moving in a periodic field of force, and subject also

to the usually assumed type of viscous resistance, may be written in the following form,

$$\ddot{U} + k\dot{U} + 2af'(t)F(U) = 0, \quad . \quad . \quad . \quad (1)$$

where $F(U)$ gives the distribution of the field, $f(t)$ its variability with respect to time, and $2a$ is a constant. If we are dealing with oscillations about a position that would be one of stable equilibrium if the field were constant, $F(U)$ may as an approximation be put equal to U. We then have

$$\ddot{U} + k\dot{U} + 2af(t)U = 0. \quad . \quad . \quad . \quad . \quad (2)$$

In the experiments described above, the periodicity of $f(t)$ is the same as that of the intermittence of the exciting current. If an alternating current had been used, the frequency of $f(t)$ would have been double that of the alternations. In any case we may write

$$af(t) = a_1 \sin nt + a_2 \sin 2nt + a_3 \sin 3nt + \text{&c.}$$
$$+ b_0 + b_1 \cos nt + b_2 \cos 2nt + b_3 \cos 3nt + \text{&c.} \quad . \quad (3)$$

Since U is shown to be periodic by experiment, we may write

$$U = A_1 \sin pt + A_2 \sin 2pt + A_3 \sin 3pt + \text{&c.}$$
$$+ B_0 + B_1 \cos pt + B_3 \cos 2pt + B_3 \cos 3pt + \text{&c.} \quad (4)$$

As a typical example of the even types of maintenance, we may take the cases in which $n = 4p$. We have

$$af(t) = a_1 \sin 4pt + a_2 \sin 8pt + a_3 \sin 12pt + \text{&c.}$$
$$+ b_0 + b_1 \cos 4pt + b_2 \cos 8pt + b_3 \cos 12pt + \text{&c.} \quad (5)$$

In this case, and also in the case of the second, sixth, and in fact in all the *even* types of maintenance, we find that the quantities A_2, A_4, A_6, &c., and B_0, B_2, B_4, &c., do not enter into the equations containing A_1 and B_1. We therefore write them all equal to zero. The significance of this is that with the *even* types of vibration maintained by a periodic field of force, the *even harmonics are all absent from the maintained motion*. This result is fully verified by a reference to the vibration-curves of the 2nd, 4th, and 6th types shown in figs. 2, 4, and 6, Pl. II. It will be seen that the vibratory motion of the armature-wheel has that type of symmetry so familiar in alternating current curves, in which all the even harmonics are absent. In other words, the image of one-half of the curve above the zero axis, as seen by reflexion in a mirror placed parallel to this axis, is exactly similar to the other half below it.

Substituting now the odd terms alone left on the right-hand side of (4), for U in equation (2), we have the following series of equations :—

$$-(b_0-p^2)A_1 + kpB_1 = -b_1A_3 + a_1B_3 + b_1A_5 - a_1B_5 - \&c. + \&c.$$

$$-(b_0-p^2)B_1 - kpA_1 = a_1A_3 + b_1B_3 + a_1A_5 + b_1B_5 + \&c. + \&c.$$

$$-(b_0-9p^2)A_3 + 3kpB_3 = -b_1A_1 + a_1B_1 - b_2A_5 + a_2B_5 + \&c. - \&c.$$

$$-(b_0-9p^2)B_3 - 3kpA_3 = a_1A_1 + b_1B_1 + a_2A_5 + b_2B_5 + \&c. + \&c. \quad (6)$$

and so on.

Evidently, the possibility of this being a consistent set of convergent equations depends upon the suitability of the values assigned to the constants k, p, b_0, a_1, b_1, &c.

It is not possible here to enter into a complete discussion of the solution of these equations. One point is, however, noteworthy. From the first two of the set of equations given above, it will be seen that such of the *harmonics* in the steady motion of the system as are present serve as the vehicles for the supply of the energy requisite for the maintenance of the fundamental part of the motion. Paradoxically enough, the frequency of none of these harmonics is the same as that of the field.

We now proceed to consider the odd types of vibration, *i. e.* the 1st, the 3rd, &c. Taking the 3rd as a typical case, we put $n = 3p$ and get

$$af(t) = a_1 \sin 3pt + a_2 \sin 6pt + a_3 \sin 9pt + \&c.$$

$$+ b_0 + b_1 \cos 3pt + b_2 \cos 6pt + b_3 \cos 9pt + \&c. \quad . \quad (7)$$

Substituting (4) and (7) in equation (2) and equating the coefficients of sine and cosine terms of various periodicities to zero, we find that the quantities A_3, A_6, A_9, &c. and B_0, B_3, B_6, B_9, &c., do not enter into the equations containing A_1 and B_1. We therefore write them all equal to zero. The significance of this is that the maintained motion contains no harmonics the frequency of which is the same as, or any multiple of the frequency of the periodic field of force. This remarkable result is verified by a reference to fig. 3, Pl. II. from which it is seen, that the vibration curve is roughly similar to that of the motion of a trisection point of a string bowed near the end, the 3rd component, the 6th, the 9th, &c., being absent at the point of observation.

We then obtain the following set of relations by substitution :

$$- (b_0 - p^2)A_1 + kpB_1 = -b_1A_2 + a_1B_2 + b_1A_4 - a_1B_4 - \text{ \&c.}$$

$$- (b_0 - p^2)B_1 - kpA_1 = a_1A_2 + b_1B_2 + a_1A_4 + b_1B_4 + \text{ \&c.}$$

$$- (b_1 - 4p^2)A_2 + 2kpB_2 = -b_1A_1 + a_1B_1 + b_1A_5 - a_1B_5 + \text{ \&c.}$$

$$- (b_0 - 4p^2)B_2 - 2kpA_2 = a_1A_1 + b_1B_1 + a_1A_5 + b_1B_5 + \text{ \&c.} \quad (8)$$

and so on.

It must be remembered that these relations are all only approximate, as $F(U)$ in general contains powers of U higher than the first which we have neglected, and which no doubt must be taken into account in framing a more complete theory. The general remarks made above with reference to equation (6) apply here also.

The exact character of the vibratory motion maintained by the periodic field of force in any case, depends upon the form of the functions $F(U)$ and $f(t)$ which determine respectively the disposition of the field and its variability with respect to time. One very simple and important form of $f(t)$ is that in which the field is of an impulsive character, in other words is of great strength for a very short interval of time comprised in its period of variation, and during the rest of the period is zero or nearly zero. Such a type of variation is not merely a mathematical possibility. In actual experiment, when a fork-interrupter is used to render the current passing through the electromagnet intermittent, the magnetization of the latter subsists only during the small fraction of the period during which the current flows and at other times is practically zero. When the current is flowing the acceleration is considerable : at other times, the acceleration is nearly zero, and the velocity practically constant. These features are distinctly shown in all the vibration-curves (except those of the first type) reproduced in Pl. II., the sudden bends in the curves corresponding roughly to the extreme outward swings of the fork, *i. e.* to the instants when the magnetizing current was a maximum. It seems possible that a simpler mathematical treatment than that given above might be sufficient to discuss the phenomena of the maintenance of vibrations by a periodic field of force when the periodicity of the field is of the "impulsive" type ; in other words, when the dynamical system is subject to periodic impulsive "springs," one, two, three or more of which occur at regular intervals during each complete period of the vibration of the system.

These experiments on vibrations maintained by a periodic

field of force are very well suited for lecture demonstration, as the Lissajous figures obtained by the method described above can be projected on the screen on a large scale, and form a most convincing demonstration of the fact that the frequency of the maintained motion is an exact sub-multiple of the frequency of the exciting current.

On Synchronous Rotation under Simple Excitation.

It is well known that with an intermittent current passing through its electromagnet, the synchronous motor can maintain itself in "uniform" rotation, when for every period of the current, one tooth in the armature-wheel passes each pole of the electromagnet. In other words, the number of teeth passing per second is the same as the frequency of the intermittent current. From a dynamical point of view it is of interest, therefore, to investigate whether the motor could run itself successfully at any speeds other than the "synchronous" speed. Some preliminary trials with the motor unassisted by any independent driving proved very encouraging. The phonic wheel I have is mounted on ball-bearings, and runs very lightly when the large stroboscopic disk usually kept fixed upon it is taken off, and there is no current passing through the motor. When a continuous or intermittent current is flowing through the motor, the latter does not, however, run very lightly, being subject to very large electromagnetic damping, apparently due to Foucault currents in the iron. In the preliminary trials, however, I found that, using the intermittent unidirectional current from an interrupter-fork of frequency 60, the motor could run successfully of itself at *half* the synchronous speed, *i. e.* with 30 teeth passing per second. It of course ran very well at the usual synchronous speed, *i. e.* with 60 teeth passing per second. By increasing the speed, it was found that the motor could also run well of itself at *double* the synchronous speed, *i. e.* with 120 teeth passing per second. Using an interrupter-fork of low frequency (23·5 per second) the motor, it was found, could also run of itself at *triple* the synchronous speed. No certain indication was, however, obtained of the intermediate speeds, *i. e.* $1\frac{1}{2}$ and $2\frac{1}{2}$ times respectively the synchronous speed.

To test these points, therefore, independent driving was provided. This was very satisfactorily obtained by fixing a small vertical water-wheel to the end of the axis of the motor and directing a jet of water against it. The water-wheel was boxed in to prevent any splashing of water on the observer. By regulating the tap leading up to the jet, the

velocity of the latter could be adjusted. The speed of the phonic wheel was ascertained by an optical method, *i. e.* by observing the rim of the wheel as seen reflected in a mirror attached to the prong of the interrupter-fork. When the motor "bites," the pattern seen becomes stationary and remains so for long intervals of time or even indefinitely, and the speed of the wheel can be inferred at once from the nature of the pattern seen.

It was found in these trials that the motor could "bite" and run at the following speeds. (Frequency of interrupter 60 per sec.)

(*a*) $\frac{1}{2}$ the synchronous speed : stationary pattern of rim of moving wheel seen as a single sine-curve : wavelength $\frac{1}{2}$ the interval between teeth. Number of teeth passing electromagnet per second = 30.

(*b*) Synchronous speed : stationary pattern of rim of moving wheel seen as a sine-curve, wave-length = interval between teeth. Number of teeth passing electromagnet per second = 60.

(*c*) $1\frac{1}{2}$ times the synchronous speed : stationary pattern of rim of wheel seen as *three* interlacing waves. Number of teeth passing electromagnet per second = 90.

(*d*) 2 times the synchronous speed : stationary pattern seen as *two* interlacing curves. Number of teeth passing per second = 120.

(*e*) $2\frac{1}{2}$ times the synchronous speed : this was only obtained with difficulty. Number of teeth passing per second = 150.

(*f*) 3 times the synchronous speed : stationary pattern seen as *three* interlacing curves. Very satisfactory running. Number of teeth per second = 180.

(*g*) 4 times the synchronous speed : stationary pattern seen as 4 interlacing curves. Number of teeth per second = 240.

(*h*) 5 times the synchronous speed : stationary pattern seen as 5 interlacing curves. Number of teeth per second = 300.

The outstanding fact of observation is that while speeds which are equal to the "synchronous" speed or any integral multiple of it are readily maintained, only the first two or three members of the other series (*i. e.* having ratios $\frac{1}{2}$, $1\frac{1}{2}$, &c. to the synchronous speed) can be obtained, and the "grip" of the wheel by the periodic magnetic forces, *i. e.* the stability of the motion, is hardly so great as in the integral

series.   This fact may be explained in the following general manner.

We may assume, to begin with, that the independent driving is less powerful than that required to overcome resistances, so that the wheel is a little *behind* the correct phases.   In the case of the integral series, one or two or more teeth pass for every intermittence of the current, the wheel being in the same relative position, whatever this may be, to the electromagnet, at each phase of maximum magnetization of the latter.   This is not, however, the case with the fractional speeds.   It is only at every *alternate* phase of maximum magnetization that the wheel assumes the same position (whatever this may be) relative to the electromagnet. At the intermediate phases, it is displaced through a distance approximately equal to half the interval between the teeth. Whereas with the integral series, *every* phase of maximum magnetization *assists* the rotation, in the fractional series the wheel is alternately assisted and retarded by the successive phases of maximum magnetization, and it is the *net* effect of assistance that we perceive, this being of course comparatively small.

As the synchronous, half-synchronous, and double-synchronous speeds can all be readily maintained without independent driving, they can be very effectively exhibited as lecture experiments by lantern projection in the following way.   The synchronous motor (which is quite small and light when the stroboscopic disk is removed) is placed on the horizontal stage of the lantern and the rim of the wheel is focussed on the screen.   In front of the projection prism, where the image of the source of light is formed, is placed the fork-interrupter with the necessary device for intermittent illumination fitted to its prongs.   When these are set into vibration and the synchronous motor is set in rotation, the " pattern " corresponding to the maintained speed becomes visible on the screen, and the effect of reversing the direction of rotation can also be demonstrated.

We now proceed to discuss the mathematical theory of the maintenance of uniform rotation in each of these cases. The first step is obviously to show that with the assumed velocity of rotation, the attractive forces acting on the disk communicate sufficient energy to it to balance the loss due to frictional forces.   Taking the line joining the poles as the axis of x, the position of the wheel at any instant may be defined by the angle θ which a diameter of the wheel passing through a given pair of teeth makes with the axis of reference. If n is the number of teeth in the wheel, the couple acting

on the latter for any given field strength at the poles is obviously a periodic function of $n\theta$ which vanishes when $\theta = \dfrac{2\pi r}{n}$, and also when $\theta = \dfrac{2\pi(r+\frac{1}{2})}{n}$, where r is any integer.

We therefore write

Couple = Field strength $\times$ $[a_1 \sin n\theta + a_2 \sin 2n\theta + a_3 \sin 3n\theta + \&\text{c.}]$

$=$ Field strength $\times f(n\theta)$ say,

where the terms a_1, a_2, a_3, &c. rapidly diminish in amplitude. It will be seen that the cosine terms are absent. Since the field strength is periodic, we may write the expression for the couple acting on the wheel thus

Couple $= \mathrm{L}f'(n\theta)\,[b_1 \sin\,(pt+\epsilon_1) + b_2 \sin\,(2pt+\epsilon_2) + \&\text{c.}]$

$= \mathrm{L}f'(n\theta)\,\mathrm{F}(t)$, say.

The work done by the couple in any number of revolutions

$$= \int \mathrm{L}f'(n\theta)\,\mathrm{F}(t)\,dt.$$

It is obvious that this integral after any number of complete revolutions is zero, except in any of the following cases, when it has a finite value proportional to and increasing with t; *i. e.* when

$$n\theta = pt \text{ or } 2pt \text{ or } 3pt \text{ or } 4pt \text{ and so on,}$$

or when

$$2n\theta = pt \text{ or } 2pt \text{ or } 3pt \text{ or } 4pt \text{ and so on,}$$

or when

$$3n\theta = pt \text{ or } 2pt \text{ and so on.}$$

It is therefore a necessary but not, of course, always a sufficient condition for uniform rotation to be possible that one or more of the above relations should be satisfied. The first series corresponds to the synchronous speed and multiples of the synchronous speed. These have been observed experimentally by me up to the fifth at least. The second series includes the above and also the half-synchronous speed and odd multiples of the same. These latter have also been observed by me up to the fifth odd multiple. Since a_2 is much smaller than a_1, the relative feebleness of the maintenance of the half-speeds observed in experiment will readily be understood.

The third series has not so far been noticed in experiment.

It is obvious that the maintaining forces in it should be excessively feeble compared with the first or the second. Perhaps experiments with interrupter-forks of higher frequencies and independent driving of the motor may succeed in showing the existence of controlled rotation-speeds at these ratios.

Combinational Rotation-speeds under Double Excitation.

When the electromagnet of the synchronous motor is excited simultaneously by the intermittent currents from two separate interrupter-forks having different frequencies, maintenance of uniform rotation is possible not only at the various speeds related to the synchronous speeds due to either of the intermittent currents acting by itself, but also at speeds related jointly to the frequencies of the two currents.

The preliminary experiments on this point were made without the assistance of any independent driving of the motor, and it was found at once that differential rotation of the motor was easily maintained, the number of teeth passing per second being equal to the difference of the frequencies of the two interrupter-forks.

When the " differentially " revolving wheel was examined by reflexion in mirrors attached to the prongs of the two interrupter-forks, it was found that the patterns seen in neither of them were stationary. They were found to be moving steadily forward or backward with a definite speed, with occasional slight to and fro oscillations superposed thereon. This continuous rotation of the patterns seen was obviously due to the fact that the frequencies of the forks and their difference did not bear any simple arithmetical ratios to each other, and it enabled a rotation-speed maintained by joint action to be distinguished by mere inspection from one maintained by either of the two currents separately.

Using this optical method, and assisting the rotation of the motor with independent driving by a water-motor, various other combinational speeds were found to be maintained. Of these, the most powerfully and steadily maintained was the simple summational rotation. The summationals and differentials of the second series, *i. e.* those in which the half-frequencies of the fork enter, were also noticed. The rotation-speeds were determined by actual counting and a stop-watch.

The mathematical theory of these combinational speeds is very similar to that given for the case of excitation by one periodic current. For the field strength in this case is also

a periodic function of the time, and the function $F(t)$ which expresses its value at any instant may be expanded in the following form

$$F(t) = a \, \Sigma\Sigma \, b \sin \left[(rp_1 \pm sp_2)t + E \right],$$

where $p_1/2\pi$ and $p_2/2\pi$ are the frequencies of the two interrupters, and r, s are any two positive integers. Using the same notation as before, we find that in any complete number of revolutions, a finite amount of energy proportional to the time is communicated to the wheel only in any one of the following sets of cases :

$$n\theta = (rp_1 \pm sp_2)t,$$

or
$$2n\theta = (rp_1 \pm sp_2)t,$$

or
$$3n\theta = (rp_1 \pm sp_2)t,$$

and so on.

The cases actually observed in which rotation is maintained fall within the first two of the sets given above.

Summary and Conclusions.

The vibrations of a dynamical system maintained by a periodic field of force have been investigated experimentally and theoretically, and it is shown that they form a new class of resonance-vibrations, in which the frequency of the maintained motion is any sub-multiple of the frequency of the exciting force. The possible speeds of synchronous rotation of a motor of the attracted-iron type under simple and double excitation are also investigated. The experiments and observations described in the present paper were carried out in the Physical Laboratory of the Indian Association for the Cultivation of Science, Calcutta, where further work on the dynamics of vibration is now in progress. One very interesting case which has been worked out is that of the Combinational vibrations of a system maintained by subjecting it simultaneously to two simple harmonic forces varying its spring. This is experimentally realized by attaching a stretched string at its two extremities to the prongs of two tuning-forks of different periods, the directions of motion of which are parallel to the string. If M and N are the frequencies of the forks, it is found that the string is set into vigorous transverse oscillation if its tension is so adjusted that the natural frequency is nearly equal to $\frac{1}{2}(Mm + Nn)$, where m and n are integers. Further details of this investigation will be published in due course.

III. *On the Ideal Refractivities of Gases.* *By* WILLIAM JACOB JONES *and* JAMES RIDDICK PARTINGTON, *Assistant Lecturers in Chemistry, Manchester University* [*].

THE formula deduced by Lorentz [†] and by Lorenz [‡]

$$\frac{\mu^2-1}{\mu^2+2}\cdot\frac{1}{d}=\kappa \text{ (a constant)} = \frac{\mu+1}{\mu^2+2}\cdot\frac{\mu-1}{d}, \quad . \quad . \quad (1)$$

where μ denotes the refractive index of a given substance for a given wave-length, and d its density, expresses very accurately the observed relations over a very wide range of densities. When μ is nearly equal to unity, as is the case with gases, $(\mu+1)/(\mu^2+2)$ approximates to 2/3, and formula (1) degenerates into the formula of Gladstone and Dale [§]:

$$\frac{\mu-1}{d}=k \text{ (a constant)}. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

We shall designate the excess of the refractive index of a gas over unity, *i. e.* $\mu-1$, its *refractivity*. The refractivity is therefore the value of k for unit density.

In their calculations of refractivities from the experimental results, investigators have, with the exception of C. Cuthbertson and E. P. Metcalfe [∥], and L. Stuckert [¶], failed to realise the necessity for taking into account the deviations of the gases employed from the ideal state.

Now the relation between temperature, pressure, and volume of a gas is at pressures less than 5 atmospheres very accurately expressed (at least in the case of permanent gases, and with very close approximation in the case of less perfect gases) by the characteristic equation of D. Berthelot [**]:

$$\left(p+\frac{a}{T_c^2}\right)(v-b)=RT, \quad . \quad . \quad . \quad . \quad (3)$$

where

$$a=\frac{27}{64}R^2\frac{T_c^3}{p_c}; \quad b=\frac{v_c}{4};$$

T_c, p_c, and v_c being the critical constants. If we consider a

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* Communicated by the Authors.
† Lorentz, Wied. *Ann.* ix. p. 641 (1880).
‡ Lorenz, *ibid.* xi. p. 70 (1880).
§ Gladstone and Dale, Phil. Trans. cxlviii. p. 887 (1858).
∥ C. Cuthbertson and E. P. Metcalfe, Proc. Roy. Soc. A. lxxx. p. 406 (1908).
¶ L. Stuckert, *Zeitschr. für Elektrochem.* xvi. p. 37 (1910).
** D. Berthelot, *Mém. du Bureau internat. des poids et mesures*, xiii. (1907).

gram-molecular mass, M, of a gas enclosed in a volume v, we have

$$d = \frac{M}{v} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Equations (2), (3), and (4) then enable us to express the variation of μ for a given gas for a definite wave-length, with temperature and pressure ; for from (2) and (4) we have

$$v = \frac{Mk}{\mu - 1}, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and by substituting the value of v from (5) in (3) we further have :

$$\left(p + \frac{a}{\dfrac{TM^2k^2}{(\mu-1)^2}} \right)\left(\frac{Mk}{\mu - 1} - b \right) = RT. \quad . \quad . \quad (6)$$

If the value of μ for a given wave-length for a gas is known at a standard temperature and pressure, and, in addition, the critical constants of the gas, then all the magnitudes in (6) are known with the exception of k. The value of k is then determined by solution of (6). If this value of k is then substituted in (6) we obtain a cubic equation in $(\mu - 1)$, the solution of which gives the value of μ at any desired temperature and pressure. This equation cannot, however, hold strictly up to the critical point, where the applicability of Berthelot's equation fails [*].

It is easily seen from the theoretical considerations, on which the Lorentz-Lorenz equation is based, that the problem is complicated by the deviations of real gases from Avogadro's hypothesis. D. Berthelot [†] has shown that these deviations lead to the introduction of a correcting term, which, for a given temperature and pressure, can be calculated from his characteristic equation. This equation then assumes the form

$$p \cdot v = R \cdot T \cdot \left[1 + \frac{9}{128} \cdot \pi \cdot \tau(1 - 6\tau)^2 \right], \quad . \quad . \quad (7)$$

where R denotes the value of the gas-constant for the particular choice of the units of p and of v; π and τ denote the ratios p/p_c and T_c/T respectively, where p_c and T_c denote the critical pressure and critical temperature respectively.

[*] *Cf.* Nernst, *Theoretische Chemie,* 7th edit. p. 241 (1913).
[†] Berthelot, *loc. cit.* p. 52 ; Nernst, *loc. cit.*

If we denote the expression

$$1+\frac{9}{128}\cdot\pi\cdot\tau\,(1-6\tau^2) \quad . \quad . \quad . \quad . \quad . \quad (8)$$

by ϕ we have from (7) and (5)

$$\frac{p\cdot k\cdot M}{\mu-1}=\phi\cdot R\cdot T. \quad . \quad . \quad . \quad . \quad (9)$$

For a low pressure p_0, the factor ϕ obviously approaches unity, and, if μ_0 denote the refractive index of the gas at the pressure p_0, we have

$$\frac{p_0\cdot k\cdot M}{\mu_0-1}=R\cdot T. \quad . \quad . \quad . \quad . \quad (10)$$

Dividing (9) by (10) we obtain

$$\frac{p}{p_0}\cdot\frac{\mu_0-1}{\mu-1}=\phi. \quad . \quad . \quad \quad . \quad (11)$$

If for a second gas, for which the value of

$$1+\frac{9}{128}\cdot\pi'\cdot\tau'\cdot(1-6\tau'^2)$$

at the same standard pressure, p, and temperature, T, is denoted by ϕ', the values of the refractive indices are μ' and μ_0' at p and p_0 respectively, then

$$\frac{p}{p_0}\cdot\frac{\mu_0'-1}{\mu'-1}=\phi'. \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Whence dividing (12) by (11) we eliminate p/p_0, and obtain

$$\frac{\mu'-1}{\mu_0'-1}\cdot\phi'=\frac{\mu-1}{\mu_0-1}\cdot\phi. \quad . \quad . \quad . \quad (13)$$

The experimental determinations of the refractive indices of gases, at normal temperature and pressure, have usually been made by interference methods involving the counting of the number of bands which cross the field of view on subjecting the gas to small changes of pressure. Strictly speaking each of these determinations would require correction for the changes of pressure from the normal value. Since, however, these pressure-changes were inconsiderable, it is quite legitimate to assume that the values of the refractive indices, as given by the several investigators, represent the values at normal temperature and pressure. These

values, however, still require correction for the deviation from the ideal state shown at normal temperature and pressure by the gas. We would nevertheless urge that in future investigations greater attention be paid to the deviations of the gases from the ideal state within the previously referred to pressure-changes. It is obvious from equation (13) that for any number of gases $[1], [2], [3], \ldots$ &c.

$$_1\mu_0 - 1 : {_2}\mu_0 - 1 : {_3}\mu_0 - 1 : \ldots \ldots$$
$$= \phi_1({_1}\mu - 1) : \phi_2({_2}\mu - 1) : \phi_3({_3}\mu - 1) : \ldots$$
$$\ldots \quad (14)$$

where $({_1}\mu_0 - 1)$, $({_2}\mu_0 - 1)$, $\ldots$ &c. represent the ideal refractivities, corrected for the deviations of the gases from Avogadro's hypothesis, expressed in terms of the refractivities of the gases at normal temperature and pressure and of the critical constants of the several gases.

In Table I. are given the mean uncorrected values of the refractivities at normal temperature and pressure for the several wave-lengths indicated, duly weighted after consideration of the original memoirs, the values of ϕ, and the corrected ideal refractivities $(\mu_0 - 1)$.

TABLE I.

Gas.	Wave-length in mm. $\times 10^6$.	Refractivity at 0° C. and 760 mm. Hg. $(\mu - 1) 10^7$.	ϕ.	Ideal Refractivity $(\mu_0 - 1) 10^7$.
Hydrogen	436	1412	1·00051	1413
,,	486	1406	1·00051	1407
,,	578	1391	1·00051	1392
,,	589	1392	1·00051	1393
,,	656	1387	1·00051	1388
Air	436	2965	0·99964	2964
,,	486	2948	0·99964	2947
,,	578	2927	0·99964	2926
,,	589	2926	0·99964	2925
,,	656	2916	0·99964	2915
Oxygen	436	2747	0·99927	2745
,,	486	2735	0·99927	2733
,,	578	2706	0·99927	2704
,,	589	2711	0·99927	2709
,,	656	2697	0·99927	2695
Nitrogen	436	3020	0·99972	3019
,,	486	3012	0·99972	3011
,,	578	2976	0·99972	2975
,,	589	2976	0·99972	2975
,,	656	2982	0·99972	2981
Argon	436	2851	0·99932	2849
,,	486	2838	0·99932	2836
,,	578	2803	0·99932	2801
,,	644	2796	0·99932	2794

Gas.	Wave-length in mm. $\times 10^6$.	Refractivity at 0° C. and 760 mm. Hg. $(\mu-1)\,10^7$.	ϕ.	Ideal Refractivity $(\mu_0-1)\,10^7$.
Krypton	486	4318	0·99744	4307
,, ...	578	4276	0·99744	4265
,, ...	671	4253	0·99744	4242
Xenon	486	7130	0·99266	7078
,, ...	578	7030	0·99266	6978
,, ...	671	7007	0·99266	6956
Carbon monoxide........	436	3420	0·99959	3419
,, ...	589	3350	0·99959	3349
Carbon dioxide	436	4575	0·99308	4544
,, ...	589	4498	0·99308	4467
,, ...	671	4470	0·99308	4439
Sulphur dioxide	436	6960	0·98040	6824
,, ...	546	6820	0·98040	6687
,, ...	589	6760	0·98040	6628
,, ...	671	6610	0·98040	6481
Hydrogen sulphide	486	...	0·98913	6498
,, ...	546	...	0·98913	6428
,, ...	579	...	0·98913	6400
,, ...	671	...	0·98913	6351
Nitrous oxide	589	5160	0·99267	5122
Nitric oxide	589	2950	0·99892	2947
Ammonia	589	3790	0·98891	3748
Cyanogen	436	8710	0·97999	8536
,, ...	671	8430	0·97999	8261
Methane	436	4500	0·99843	4492
,, ...	578	4420	0·99843	4413
,, ...	589	4410	0·99843	4403
,, ...	656	4400	0·99843	4393
Ethane	436	7820	0·98924	7736
,, ...	546	7690	0·98924	7607
,, ...	671	7630	0·98924	7548
Ethylene	436	7430	0·99222	7371
,, ...	671	7170	0·99222	7113
Acetylene	436	6190	0·99179	6139
,, ...	671	5980	0·99179	5930
Chlorine	589	7730	0·98417	7608
Hydrogen chloride	589	4470	0·99272	4437

In Table II. the dispersions of a number of gases have been expressed in terms of the ideal refractions for wave-length 589.

TABLE II.

Wave-length	436	486	656	671
Gas.				
Hydrogen	+20	+14	−5	—
Air	+39	+22	−10	—
Oxygen	+36	+24	−14	—
Nitrogen	+44	+36	—	—
Sulphur dioxide	+196	—	—	−147
Methane	+89	—	−10	—

In Table III. are given the values of the dielectric con‾
stant ϵ for several gases at normal temperature and pressure,
together with the values of $\sqrt{\epsilon}$ which on the electromagnetic
theory of light should, for insulating media with very small
magnetic susceptibility, when corrections for dispersion are
taken into account, be equal to the refractive indices of the
said gases. The measurements of the dielectric constants
have all been executed with frequencies exceeding 10^6, so
that they may be regarded as referring directly to waves
of infinite length. Although strictly speaking a small
correction for the deviations from the gas laws should be
applied to the values of the dielectric constants, which
refer to normal temperature and pressure, its magnitude
does not, in $\sqrt{\epsilon}$, exceed the limits of experimental errors.

For the purpose of comparison the values of the refractive
indices should strictly speaking be extrapolated to infinite
wave-length. Since in all cases we are dealing with normal
dispersion, this procedure would lead to smaller values of
the refractive indices. As a matter of fact, however, the
higher values of the refractive indices, corresponding to the
shorter wave-lengths, are in better agreement with the ob-
served values of $\sqrt{\epsilon}$ than are the extrapolated values.
Assuming the correctness of the usual dispersion formulæ,
and the theoretical relation between the refractive index and
the dielectric constant, this result would seem to indicate that
the determinations of the latter are affected by some constant
error. It would seem more probable, in view of the better
agreement among the values of the refractive indices given
by different observers, than among the values of the dielectric
constants, that the origin of the discrepancy is to be sought
in the latter rather than in the former.

TABLE III.

Gas.	ϵ.	$\sqrt{\epsilon}$.	μ_0.
Hydrogen	1·000264	1·000132	1·000139 ($\lambda=656$)
Air	1·000590	1·000295	1·000292 ($\lambda=656$)
Oxygen	1·000547	1·000274	1·000270 ($\lambda=656$)
Nitrogen	1·000606	1·000303	1·000298 ($\lambda=656$)
Carbon monoxide	1·000693	1·000347	1·000335 ($\lambda=589$)
Carbon dioxide	1·000987	1·000494	1·000444 ($\lambda=671$)
Sulphur dioxide	1·000993	1·000497	1·000648 ($\lambda=671$)
Nitrous oxide	1·000940	1·000470	1·000512 ($\lambda=589$)
Ammonia	1·000610	1·000305	1·000375 ($\lambda=589$)
Methane	1·000949	1·000475	1·000439 ($\lambda=656$)
Ethylene	1·001384	1·000692	1·000711 ($\lambda=671$)

A question of great chemical interest is that of the influence of the constitution of the molecule on the refractivity. This has already been studied by Brühl*, who from a consideration of the uncorrected values arrived at the conclusion that: " ... die Molekularrefraktion der Gase ist keine rein additive, sondern eine unter gewissen Umständen deutlich konstitutive Eigenschaft derselben." A similar view was later expressed by C. and M. Cuthbertson †. Such a conclusion could not, however, be final until account had been taken of the reduction to the ideal state. In Table IV. are given the values of the refractivities of a few gases calculated from those of their simpler constituents, and the observed refractivities of the same gases, all reduced to the ideal state.

<div align="center">TABLE IV.</div>

Gas.	$(\mu_0-1)\,10^7$ calc.	$(\mu_0-1)\,10^7$ obs.
HCl (H+Cl)	4550	4437
NH₃ (N+3H)	3577	3748
CO₂ (CO+O)	3029	4467
N₂O (NO+N)	5656	5122
(2N+O)	4329	
NO (N+O)	2273	2947
C₂H₄ (C₂H₂+2H)	7552	7371
CH₄ (C₂H₆+2H)	4049	4492
(C₂H₂+6H)	5216	
C₂H₆ (C₂H₂+4H)	9965	7736

Some additive relation underlying the whole series is immediately apparent. In the cases where the elements of the constituent compound gases (*e. g.* CO) are united by different linkages from those in the more complex gases (*e. g.* CO_2), the divergence from the additive relation, however, becomes considerable. Thus, if the refractivity of methane be calculated from that of the saturated hydrocarbon ethane, it is in much better agreement with the observed value than when it is calculated from that of the unsaturated hydrocarbon acetylene.

The results collected in Table IV. show that, even with the ideal refractivities, the conclusion of Brühl still holds good.

* J. W. Brühl, *Zeitschr. physik. Chem.* vii. p. 1 (1891).

† C. and M. Cuthbertson, Proc. Roy. Soc. A. lxxxiii. p. 171 (1909). These authors applied a correction in the cases of sulphur dioxide and hydrogen sulphide by multiplying the refractivity by the ratios of the theoretical to the observed densities.

Summary.

The refractivities of several gases have been referred to the ideal state by means of the characteristic equation of D. Berthelot. The corrected values are called the "ideal refractivities."

A comparison has been instituted between the ideal refractivities and the dielectric constants of the gases.

The conclusion of Brühl that refractivity is highly additive in character has been confirmed in the case of the ideal refractivities.

IV. *A Theory of Supersaturation.* By W. J. JONES, *M.Sc.,* and J. R. PARTINGTON, *M.Sc., Assistant Lecturers in Chemistry, Manchester University* *.

THE solubility s of a given solid substance in a given solvent depends on the temperature, the pressure, and the size of the solid particles in contact with the saturated solution. If we consider spherical particles of radius r, we have

$$s = f(\mathrm{T, P}, r), \quad \ldots \ldots \ldots \quad (1)$$

where T is the temperature and P the pressure.

The problem of the surface energy between a solid and its saturated solution was first systematically treated by J. W. Gibbs †, and from a different standpoint by J. J. Thomson ‡. The more recent investigations of Ostwald, Hulett, and Freundlich have been considered in two papers by W. J. Jones §, in which the theory is applied to various special cases.

The importance of the theory of surface energy in the study of supersaturation does not, however, appear to have been realized. The results of the investigations referred to may be summarized in the formula

$$\frac{\mathrm{RT}}{\mathrm{M}} \log_e \frac{s_2}{s_1} = \frac{2\sigma}{\rho}\left(\frac{1}{r_2} - \frac{1}{r_1}\right), \quad \ldots \ldots \quad (2)$$

where R is the gas-constant, T the absolute temperature, M the molecular weight of the *dissolved* substance, σ the energy per unit area of the surface of separation of the solid and the solution, ρ the density of the solid, s_1 and s_2 the

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* Communicated by the Authors.
† 'Scientific Papers,' New York, i. p. 315.
‡ 'Applications of Dynamics to Physics and Chemistry,' p. 251.
§ *Zeitschr. physik. Chem.* lxxxii. p. 448 (1912); *Ann. Phys.* (4) xli. p. 441 (1913).

concentrations of the solute when spherical particles of radii r_1 and r_2 respectively are in contact with the saturated solutions. If r_2 is infinite, the corresponding value of s_2 is equal to the ordinary " solubility," which may be called the " normal solubility," and denoted by s_∞. The normal solubility is therefore the concentration of a solution in equilibrium with a plane surface of the solid solute. The difference between the solubility of spherical particles of radius r and the normal solubility is therefore given by the equation

$$\frac{RT}{M} \log_e \frac{s}{s_\infty} = \frac{2\sigma}{\rho r}. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Hence we find the value of s for any value of r in terms of s_∞:

$$\log_e s = \frac{2M\sigma}{RT\rho r} + \log_e s_\infty.$$

For $\log_e s_\infty$ we can substitute the expression *

$$\log_e s_\infty = -\frac{\lambda_0}{RT} + \frac{\alpha'}{R} \log_e T + \text{const.},$$

where $\lambda = \lambda_0 + \alpha'T$ is the heat absorbed when a gram-molecule of the solid dissolves in the nearly saturated solution ; λ_0 and α' are constants. Thence

$$s = A e^{\left(\frac{2M\sigma}{RT\rho r} - \frac{\lambda_0}{RT} + \frac{\alpha'}{R} \log_e T + k\right)}. \quad . \quad . \quad . \quad (4)$$

Over a small range of temperature, ρ is a linear function of temperature ; a closer approximation is given by the equation

$$\frac{1}{\rho} \cdot \frac{d\rho}{dT} = \alpha \text{ (a constant)}. \quad . \quad . \quad . \quad . \quad (5)$$

The value of ρ is practically independent of r.

As a first approximation σ is also a linear function of temperature †, and hence we may assume that the equation

$$\frac{1}{\sigma} \cdot \frac{d\sigma}{dT} = \beta \text{ (a constant)} \quad . \quad . \quad . \quad . \quad (6)$$

represents a closer approximation: σ is also practically independent of r.

We have now to consider how the radius of the particles in equilibrium with a given supersaturated solution (*i. e.*, a solution which contains more solute than corresponds with the normal solubility) alters with the temperature, when the

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* Hardman and Partington, Trans. Chem. Soc. xcix. p. 1769 (1911).
† Frankenheim, *Lehre von der Kohäsion*, 1836.

amount of dissolved substance remains constant. If we consider a supersaturated solution of given concentration at a temperature T, then equation (3) shows that there is a particle of definite radius r which will be in equilibrium with this solution. The size of this particle we will call the equilibrium-size. Towards particles of greater radius the solution behaves as supersaturated, *i. e.* the introduction of such particles into the solution would bring about crystallization. Towards particles of less radius the solution behaves as unsaturated, *i. e.* if such particles are introduced into the solution they dissolve. These results have been confirmed experimentally by Ostwald and by Hulett (*loc. cit.*). Now let the temperature be raised to $(T + \delta T)$. The equilibrium size will also be changed, and the alteration may be calculated as follows. Let $(r + \delta r)$ be the new equilibrium radius, and $(\sigma + \delta\sigma)$, $(\rho + \delta\rho)$ the corresponding values of the surface energy and density. Since the concentration remains practically constant,

$$s_{(T+\delta T)} = s_T \cdot \quad . \quad . \quad . \quad . \quad . \quad (7)$$

We have at the temperature $T + \delta T$,

$$S_{(T+\delta T)} = A \cdot e^{\left[\frac{2 \cdot M \cdot (\sigma + \delta\sigma)}{R(\rho + \delta\rho)(T+\delta T)(r+\delta r)} - \frac{\lambda_0}{R(T+\delta T)} + \frac{a'}{R} \cdot \log_e(T+\delta T) + k\right]}. \quad (8)$$

The exponents in equations (4) and (8) are therefore equal; and if we expand $\log \frac{T + \delta T}{T}$ in a series, and assume δT to be infinitesimally small, we have:

$$d T\left(-\frac{1}{T} + \frac{\lambda_0 \cdot \rho \cdot r}{2 \cdot T \cdot M \cdot \sigma} + \frac{a' \cdot \rho \cdot r}{2 \cdot M \cdot \sigma} \right) + \frac{d\sigma}{\sigma} - \frac{d\rho}{\rho} - \frac{dr}{r} = 0. \quad (9)$$

It is, however, known by experiment that α is approximately equal to β [*], *i. e.*,

$$\frac{d\sigma}{\sigma} - \frac{d\rho}{\rho} = 0, \quad . \quad . \quad . \quad . \quad . \quad (10)$$

or

$$\frac{\rho}{\sigma} = \text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Thence we find from equation (9):

$$d T\left(-\frac{1}{T} + \frac{k \cdot r}{T} + k_1 \cdot r \right) - \frac{dr}{r} = 0, \quad . \quad . \quad (12)$$

where

$$k = \frac{\lambda_0 \cdot \rho}{2 \cdot M \cdot \sigma}, \quad \text{and} \quad k_1 = \frac{a' \cdot \rho}{2 \cdot M \cdot \sigma}.$$

[*] Partington, 'Thermodynamics,' p. 433.

In this equation α' is small compared with $\frac{\lambda_0}{T}$, and thence k_1 may be neglected in comparison with k. Equation (12) then reads :

$$\frac{d\mathrm{T}}{dr} - \frac{\mathrm{T}}{kr^2 - r} = 0. \quad \ldots \quad (13)$$

By integration of (13) we obtain the equation on which the theory of supersaturation now proposed is based :

$$\mathrm{T} = \mathrm{C}\left(\frac{k \cdot r - 1}{k \cdot r}\right). \quad \ldots \quad (14)$$

If λ is positive, *i.e.* when heat is absorbed on dissolution of the solid in a nearly saturated solution, then the expression $\frac{kr-1}{kr} < 1$. If r is diminished, the corresponding value of T is also diminished. If, on the contrary, λ is negative (*i. e.* heat is evolved on dissolution), then $\frac{kr-1}{kr} > 1$, and in this case T increases when r is diminished.

Ordinary supersaturated solutions belong to the first type. An example of the second type ($\lambda < 0$) is furnished by a normally saturated solution of gypsum.

The constant C in equation (14) denotes the temperature at which the given concentration is equal to the concentration of the normally saturated solution, since when $r = \infty$, then $\mathrm{T} = \mathrm{C}$.

The spontaneous crystallization of supersaturated solutions of the first type, when they are cooled below a certain temperature, remains to be explained. In the sense of the theory described above, the size of the particle required to induce crystallization is smaller the lower the temperature. It may therefore be assumed that at a sufficiently low temperature the necessary size is only a relatively small multiple of the molecular size, an assumption which becomes more probable from the following considerations. In order that a particle of this size may be produced in the solution itself, it is obviously necessary that several molecules shall simultaneously collide inside a small element of volume. This leads directly to the hypothesis of de Coppet [*], according to which the formation of crystals is dependent on a " favourable collision " of the molecules concerned, and such " favourable collisions " occur all the more frequently the further the solution is removed from its state of normal saturation. An estimate of the size of particle required can

* *Ann. chim. phys.* (5) vi. p. 275 (1875).

be obtained from the results of Ostwald [*], according to which a quantity of solid solute less than 10^{-9} gram was no longer capable of bringing about the crystallization of a supersaturated solution of sodium chlorate prepared from 107 parts of salt and 100 parts of water. This corresponds with a radius of about $10\,\mu$, and this must therefore be less than the equilibrium size in equation (3). At lower temperatures very much smaller particles would, however, be active; and it is conceivable that molecular groups having radii from $0\cdot01\mu$ to $0\cdot1\mu$ could be formed by multiple molecular collisions in the solution.

A diminution of active radius would result in solutions of the second type from a rise of temperature. Such solutions should therefore crystallize spontaneously when heated above a certain temperature, which would be higher the less the supersaturation. There appear to be no quantitative experiments in this field.

In the case of ordinary supersaturated solutions, the active size of particle will be formed from a smaller number of molecules the lower the temperature. The favourable collisions will therefore change with falling temperature from higher to lower orders, and the probabilities of such collisions will then increase enormously. De Coppet seems to have regarded the diminished molecular velocity resulting from the lowering of temperature as the chief cause of the spontaneous crystallization of supersaturated solutions. In the sense of the theory now proposed, the main cause of that phenomenon is rather the variation of the equilibrium size with temperature, *i.e.* the shift of the probability of the formation of particles of active size from smaller to larger values with fall of temperature.

A rough calculation shows that the equation (14) gives results of at least the right order of magnitude, which is all that can at present be expected. If we consider a solution of Glauber's salt normally saturated at $27°$ C., then

$$\mathrm{T}_\infty = \mathrm{C} = 273 + 27 = 300.$$

Also $2\mathrm{M} = 284 = 300$ approx. In the cases which have been quantitatively examined [†], σ is of the order 10^3 erg. We can further assume that $\rho = 3$, and $\lambda_0 = 500$ cal. $= 25 \times 10^9$ erg. Then

$$k = \frac{\lambda_0 \rho}{2\mathrm{M}\sigma} = 25 \times 10^4 \text{ cm.}^{-1}.$$

[*] *Lehrb. allgem. Chem.* 2 Aufl., ii. p. 754.
[†] *Cf.* Jones, *loc. cit.*

If we assume that the active size is $r = 10^{-4}$ cm., then

$$T = 300 \left(\frac{24}{25} \right) = 284°,$$

i.e., at this temperature, or with a supercooling of 16° C., the solution would crystallize spontaneously.

The theory now described therefore leads to the following properties of supersaturated solutions:—

(1) It is possible for a solution to contain more solute than corresponds with equilibrium in contact with a plane surface of solid solute (*i. e.* large crystals of the latter).

(2) Such a " supersaturated " solution can be in equilibrium with particles of solid of a definite size. Smaller particles dissolve in the solution, larger particles bring about its crystallization.

(3) According as the solid dissolves in its nearly saturated solution with absorption or evolution of heat, the size of " active " particles of solid, *i.e.* such as induce crystallization in a given solution, decreases with fall of temperature, or rise of temperature respectively.

(4) The solution may, at a sufficiently low or high temperature, respectively, crystallize spontaneously.

V. *The Magnetic Field of an Atom in Relation to Theories of Spectral Series.* *By* H. Stanley Allen, *M.A., D.Sc.*[*]

IN the course of a discussion on the structure of the atom it was pointed out by the present writer[†] that it may be necessary to take into account not only the electrostatic, but also the magnetic forces in the neighbourhood of the atom. It was suggested[‡] that the atom might be regarded as a central core, carrying an electric charge and producing a magnetic field similar to that due to an elementary magnet, the core being surrounded by electrons in orbital motion. Such a magnetic core might arise from a spherical volume distribution of electricity rotating about a diameter with a specified angular velocity.

One of the most important questions to be considered in connexion with any atomic model is the possibility of explaining the lines in the spectra of the elements, and in particular the relations between the frequencies of the lines

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in spectral series. Nicholson* has been successful in calcu-
lating the frequencies of the lines in the nebular and coronal
spectra by employing Rutherford's model involving only
electrostatic forces. In these cases, however, only a *simple*
nucleus is dealt with. The theory put forward by Bohr† is
confessedly not dependent on the usual dynamical laws,
although it involves the calculation by ordinary mechanics
of the steady motion of the electron in the electrostatic field
of the positive nucleus. All the relations that have been
obtained between the lines in a spectrum involve the
frequency of the vibration. Lord Rayleigh‡ has pointed
out that in the case of vibrations under electric or elastic
forces it is the square of the frequency that is involved. If,
however, the vibrations take place under the action of mag-
netic forces, the acceleration, instead of being proportional
to the displacement, is proportional to the velocity of the
moving electrified particle, and relations involving the
frequency of the vibration may be obtained. A theory
based on this consideration has been put forward by Ritz§.
He assumes the existence of molecular magnets, and sup-
poses that the electron is describing a circular orbit in a
fixed plane perpendicular to the axis of the magnet. The
elementary magnets are the same for all elements. To get
the different lines of a series he supposes that a number of
the elementary magnets are placed end to end, so that the
magnetic field is due to two poles whose distance apart is
always some multiple of the length of the elementary magnet.
It is a characteristic feature of the theory of Ritz that every
spectral line is brought about by the difference of two
actions.

Empirical Formulæ for Spectral Series ‖.

It will be convenient to summarize here the empirical
formulæ that have been suggested to represent the distribu-
tion of the lines in a spectral series.

If N denote the wave number (*i. e.* the number of waves
in 1 cm.) Balmer's series for hydrogen may be written

$$N = N_0 \left(\frac{1}{4} - \frac{1}{m^2} \right),$$

where N_0 is Rydberg's "universal" constant (usually taken
as 109675) and m is a positive integer, 3, 4, 5 ... .

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* Nicholson, Monthly Notices R. A. S., 1912–1914.
† Bohr, Phil. Mag. xxvi. pp. 1, 476 (1913).
‡ Rayleigh, Phil. Mag. xliv. p. 536 (1897).
§ Ritz, *Ann. der Physik*, xxv. p. 660 (1908).
‖ See Baly's 'Spectroscopy,' Chapter xvii., 1912.

If ν denote the frequency of vibration, $\nu = Nc$, where c is the velocity of light, and the formula may be written

$$\nu = \nu_0 \left(\frac{1}{4} - \frac{1}{m^2} \right),$$

where ν_0 has the value $3 \cdot 29 \times 10^{15}$ sec.$^{-1}$. Bohr's theory identifies ν_0 with $2\pi^2 m e^4 / h^3$, the numerical agreement between the two quantities being remarkable.

In the case of elements other than hydrogen [*], more complicated formulæ have been proposed. The typical Rydberg series is of the form

$$N = N_0 \left\{ \frac{1}{(1 + \mu_0)^2} - \frac{1}{(m + \mu)^2} \right\},$$

where μ_0 and μ are fractions. This may conveniently be written

$$N = N_0 \left\{ \frac{1}{D_0{}^2} - \frac{1}{D^2} \right\}.$$

Rydberg states that the true formula should be given by writing for D some function of $m + \mu$, say $m + \mu + \dfrac{\alpha}{m + \mu}$. In commenting on this Hicks makes the following significant statement :—

"If a series is represented by $D = m + \mu + \dfrac{\alpha}{m + \mu}$ a slight alteration will represent it equally well by putting D a continued fraction, viz.

$$D = m + \mu + \cfrac{\alpha}{m + \mu + \cfrac{\alpha}{m + \mu + \ldots}},$$

in other words,

$$\frac{N_0}{D^2} = \frac{N_0}{\alpha^2} \left[\sqrt{ \left\{ \left(\frac{m + \mu}{2} \right)^2 + \alpha \right\} } - \frac{m + \mu}{2} \right]^2,$$

or $N = A - B \{ \sqrt{(m^2 + 2am + b)} - (m + a) \}^2,$

which looks quite different, and points to the frequencies depending on the roots of a quadratic" [†].

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[*] Curtis (Proc. Roy. Soc. vol. xc. p. 605, 1914) finds that the results for hydrogen may be represented by a modified Rydberg formula.

[†] Hicks, Phil. Trans. vol. ccx. p. 85 (1910). The notation of the original has been slightly modified.

Ritz[*] has obtained remarkable agreement between the observed and the calculated results by taking

$$D = m + \mu + \beta/m^2 \quad \text{or} \quad D = m + \mu + \frac{\beta}{(m+\mu)^2}.$$

Several investigators have made use of the form suggested by Moggendorf and Hicks, in which

$$D = m + \mu + \alpha/m.$$

The value of the expression N_0/D^2 for integral values of m has been called a sequence. Four sequences exist, and it has been shown by Hicks, van Lohuizen[†], and others that the majority of the lines in spectral series can be determined by the difference between two sequences.

The Magnetic Field of the Atom in the Quantum Theory of Spectral Series.

In a letter to 'Nature' (vol. xcii. p. 630, 1914) I have drawn attention to the important work of Professor Carl Størmer on the path of an electron in the magnetic field of an elementary magnet. He has investigated the motion of an electron when it is subject to the action of a central force varying inversely as the square of the distance from the centre of the magnet. Such a case would arise if the atom consisted of a magnetic core, electrically charged and surrounded by one or more electrons. Størmer finds certain remarkable periodic trajectories in the form of a circle whose plane is perpendicular to the axis of the magnet, and whose centre is at some point on that axis. If this point coincide with the centre of the magnet we obtain circular orbits in the equatorial plane of the magnet. Further there are other trajectories which never get outside closed toroidal spaces, in the case of stability, or which approach asymptotically the circle in question in the case of instability.

Let the magnetic moment of the core, considered as an elementary magnet, be M and its positive charge be E, electrostatic units being employed throughout. The equation of motion of an electron (charge e, mass m) moving, with angular velocity ω, in a circular orbit of radius r in the equatorial plane is

$$mr^3\omega^2 = Me\omega + Ee. \quad . \quad . \quad . \quad . \quad (1)$$

It must be noticed that there are two possible directions

[*] Ritz, *Phys. Zeitschr.* vol. iv. p. 406 (1903); vol. ix. pp. 244, 521 (1908).

[†] van Lohuizen, Science Abstracts, vol. xvi. no. 179 (1913).

of motion of the electron in its circular path, in the one the mechanical force due to the movement in the magnetic field is directed towards the centre, in the other away from it. These may both be included in the formula by supposing that M may be either positive or negative, the positive sign being taken when the mechanical force is directed towards the centre.

This equation is not in itself sufficient to specify the motion completely. " There is but one equation of motion, the radial one, while there are two independent variables, the speed and the radius of the orbit " (Schott, 'Electromagnetic Radiation'). In order to obtain a second equation we assume that the angular momentum can be expressed in the form

$$mr^2\omega = \tau h/2\pi, \quad . \quad . \quad . \quad . \quad (2)$$

where h is Planck's constant, and τ is a coefficient whose value is not for the present specified.

On eliminating r by means of equations (1) and (2) we obtain a quadratic equation for ω, which may be written

$$(M\omega + E)^2 = A\omega,$$

or $$M^2\omega^2 - \omega(A - 2ME) + E^2 = 0, \quad . \quad . \quad . \quad (3)$$

where $A = \dfrac{\tau^3 h^3}{8\pi^3 m e^2}.$

Remembering that M may be either positive or negative, we see that there are in general four possible values for ω and four corresponding frequencies ν, since $\omega = 2\pi\nu$.

If we divide equation (1) by the square of equation (2) we obtain the value of $\dfrac{1}{r}$ in the form

$$\frac{1}{r} = \frac{4\pi^2 m}{\tau^2 h^2} (M\omega + Ee),$$

or approximately, when the effect of the magnetic field is neglected,

$$\frac{1}{r} = \frac{4\pi^2 m Ee}{\tau^2 h^2}. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

As in Bohr's theory we consider next the work that is required to move the electron from its orbit to a position of rest at infinity. Denoting this quantity by W, we find, assuming the mass of the core large and the effect of other electrons negligible,

$$W = \frac{Ee}{r} - \frac{1}{2} mr^2\omega^2. \quad . \quad . \quad . \quad . \quad (5)$$

In Bohr's theory W is capable of being expressed by the equation

$$W = \frac{\sigma h \omega}{4\pi},$$

where σ is an integer.

Let us now put

$$U = W + \frac{Me\omega}{r} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (6)$$

$$= \frac{Ee}{r} - \frac{1}{2}mr^2\omega^2 + \frac{Me\omega}{r}.$$

Then by means of (1) we find that U reduces to $\frac{1}{2}mr^2\omega^2$, which is the kinetic energy of the electron.

Making use of (2) we see that

$$U = \frac{\tau h \omega}{4\pi} \cdot \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (7)$$

When there is no magnetic field present τ and σ become identical and $U = W$. In the presence of the magnetic field we have to take into account the small term $Me\omega/r$. We proceed to find the approximate relation between τ and σ in this case.

Combining (6) and (7) we find

$$\frac{\tau h \omega}{4\pi} = \frac{\sigma h \omega}{4\pi} + \frac{Me\omega}{r}$$

$$= \frac{\sigma h \omega}{4\pi} + \frac{4\pi^2 m M E e^2 \omega}{\tau^2 h^2}.$$

Hence

$$\tau = \sigma + \frac{16\pi^3 m M E e^2}{\tau^2 h^3}, \quad \cdot \quad \cdot \quad \cdot \quad (8)$$

or, approximately,

$$\tau = \sigma + \frac{16\pi^3 m M E e^2}{\sigma^2 h^3}$$

$$= \sigma + \frac{\delta}{\sigma^2}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (9)$$

where

$$\delta = \frac{16\pi^3 m M E e^2}{h^3}.$$

The value of W may be expressed in a form more convenient for our purpose as follows :

$$W = \frac{\sigma h \omega}{4\pi}$$

$$= \frac{\sigma h}{4\pi A}(M\omega + E)^2 \cdot \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (10)$$

Substituting the value of $\boldsymbol{\omega}$ derived from the quadratic equation (3) we find

$$W = \frac{2\pi^2 me^2 E^2 \sigma}{\tau^3 h^2} \left[\frac{A}{2ME} \pm \sqrt{\left(\frac{A}{2ME}\right)^2 - \frac{A}{ME}} \right]^2. \quad (11)$$

We now proceed to express the quantity inside the square bracket, which may be denoted by x, as a continued fraction of the form $x = \dfrac{1}{a+} \dfrac{1}{b+} \dfrac{1}{a+} \cdots$.

Since $x = \dfrac{1}{a+} \dfrac{1}{b+x}$, x is the root of the quadratic equation $ax^2 + abx - b = 0$, and therefore

$$x = -\frac{b}{2} \pm \sqrt{\left(\frac{b}{2}\right)^2 + \frac{b}{a}}.$$

So we find $a = 1$ and $b = -\dfrac{A}{ME}$.

Hence

$$W = \frac{2\pi^2 me^2 E^2 \sigma}{\tau^3 h^2} \frac{1}{\left[1 + \cfrac{1}{-\cfrac{A}{ME}+} \cdots \right]^2}, \quad \cdot \quad \cdot \quad (12)$$

or approximately

$$W = \frac{2\pi^2 me^2 E^2 \sigma}{\tau^3 h^2} \frac{1}{\left[1 - \dfrac{ME}{A} \right]^2} \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (13)$$

An examination of the numerical magnitude of the quantities involved in the term ME/A shows that in general the value of this term must be less than unity.

In Bohr's theory monochromatic radiation is supposed to be emitted during the passage from one steady state of motion of the electron to another. How this change takes place is left undetermined, but it is assumed that the amount of energy radiated, that is the difference between the energy in the first orbit and that in the second, is exactly one quantum. That is

$$h\nu = \delta W = W_2 - W_1. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (14)$$

The frequency of the radiation is therefore given by

$$\nu = \frac{2\pi^2 me^2 E^2}{h^3} \left\{ \frac{\sigma_2 x_2^2}{\tau_2^3} - \frac{\sigma_1 x_1^2}{\tau_1^3} \right\}, \quad \cdot \quad \cdot \quad \cdot \quad (15)$$

or approximately

$$\nu = \frac{2\pi^2 me^2 E^2}{h^3} \left\{ \frac{\sigma_2}{\tau_2^3 \left[1 - \dfrac{ME}{A_2} \right]^2} - \frac{\sigma_1}{\tau_1^3 \left[1 - \dfrac{ME}{A_1} \right]^2} \right\}. \quad (16)$$

Substituting the value of τ in terms of σ previously obtained, we find that the frequency is given by the approximate formula

$$\nu = \frac{2\pi^2 m e^2 \mathrm{E}^2}{h^3} \left\{ \frac{1}{\left[\sigma_2 + \dfrac{\mathrm{B}}{\sigma_2{}^2}\right]^2} - \frac{1}{\left[\sigma_1 + \dfrac{\mathrm{B}}{\sigma_1{}^2}\right]^2} \right\}, \quad (17)$$

where

$$\mathrm{B} = -\frac{8\pi^3 m \mathrm{M} \mathrm{E} e^2}{h^3} + \frac{3\delta}{2} = \frac{16\pi^3 m \mathrm{M} \mathrm{E} e^2}{h^3} = \delta.$$

We may note that equation (17) is equivalent to

$$\nu = \frac{2\pi^2 m e^2 \mathrm{E}^2}{h^3} \left\{ \frac{1}{\tau_2{}^2} - \frac{1}{\tau_1{}^2} \right\}. \quad \cdots \quad (18)$$

The formula proposed by Ritz to represent spectral series may be written

$$\nu = \nu_0 \left\{ \frac{1}{\mathrm{D}_2{}^2} - \frac{1}{\mathrm{D}_1{}^2} \right\}, \quad \cdots \quad (19)$$

where D is of the form $m + \mu + \beta/m^2$ or $m + \mu + \beta/(m+\mu)^2$, and ν_0 is the frequency corresponding to Rydberg's constant.

When $\mathrm{E} = e$, that is when the core carries a charge equivalent to the loss of one electron, the factor outside the bracket in equation (17) reduces to $2\pi^2 m e^4/h^3$, which Bohr identifies with ν_0. The bracket becomes identical in form with that in the formula of Ritz if we take $\sigma = m + \mu$ and $\delta = \beta$.

This implies that σ, instead of being an exact integer (m), as in Bohr's theory, is equal to an integer plus a certain fractional quantity μ, which depends on the element and on the particular series considered. The presence of this fractional part must be assumed; it is not explained by the action of magnetic forces.

We conclude that, on the assumptions stated, we can account for the existence of four sequences in spectral series, the denominator of each sequence being of the form proposed by Ritz, and we can determine the lines in a spectral series by the difference between two sequences.

When, however, we examine the numerical value of the constant β as given by Ritz, we find that the values obtained for the magnetic moment M by identifying Ritz's constant with the δ of our analysis are many times too large to be possible. Thus taking for illustration the case of lithium, Ritz gives for β in the principal series the value $0\cdot0257$, which would correspond with $\mathrm{M} = 4\cdot5 \times 10^{-18}$ E.M.U. The magnetic moment of the magneton is $1\cdot854 \times 10^{-21}$ E.M.U.

Thus the core of the lithium atom would have to be equivalent to about 2500 magnetons ! We are forced to the conclusion that the magnetic field can be responsible for only a small part of the term in question. The assumptions that we have been compelled to make as to the constitution of the atom, namely, that the magnetic field may be regarded as equivalent to that set up by an elementary magnet and that the electrostatic field may be treated as varying inversely as the square of the distance from the centre, involve so much simplification that we can hardly expect the result to do more than point the way towards the correct form for the expression D in the denominator of a sequence. If, for example, we treat the core of the atom as a positive nucleus surrounded by a continuous ring of negative electricity, analysis shows that the electrostatic field gives rise to a term in the expression D of the same form as δ/σ^2. Thus in the case of an element containing a large number of electrons, it may be possible to obtain an approximate formula which would agree with that proposed by Ritz (or perhaps that proposed by Hicks), but in the case of elements like helium and lithium, which contain only a few electrons, the difficulties in the way of Bohr's theory put forward by Nicholson [*] still remain serious if not insuperable.

The general conclusion that may be drawn from the present work is that the magnetic forces set up by the atom, though they may play a part in controlling and perhaps stabilising the motion of the electrons, are insufficient to account for more than a small fraction of the effect that would be necessary to give the observed distribution of lines in spectral series.

Summary.

It is shown that a formula, similar to that of Ritz, representing the distribution of lines in spectral series can be deduced from the assumptions following :—

(1) The core of an atom gives rise not only to an electrostatic field varying inversely as the square of the distance from the centre, but also to a magnetic field such as would be set up by an elementary magnet.

(2) The steady states of motion of an electron in the field of the atom are determined by the ordinary laws of electrodynamics, combined with specified assumptions as to the angular momentum and the energy of the electron.

(3) The energy of the radiation, as in Bohr's theory, is

* Nicholson, Phil. Mag. vol. xxviii. p. 90 (1914).

given out in quanta, which represent the differences between the energies in two steady states of motion.

When, however, the numerical value of the appropriate constants in the formula of Ritz is considered, it is found that the magnetic forces set up by the atom are not in themselves sufficient to account for more than a small fraction of the effect that would be necessary to give the observed distribution of lines in spectral series.

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VI. *On the Motion of the Lorentz Electron.* By G. A. SCHOTT, *B.A., D.Sc., Professor of Applied Mathematics, University College of Wales, Aberystwyth*[*].

DURING a theoretical investigation of the origin of X-rays I found it necessary to take into account the effect on the motion of the electron of the reaction due to its own radiation, and from this point of view examined some simple cases of motion in order to gain a clear idea of the result to be expected. The following communication includes these preliminary studies, but is also intended to serve as an introduction to a more complete investigation to be published later.

The Equations of Motion and Energy of the Electron.

1. The vector-equation of motion of the electron may be written in the following form [†]

$$\dot{\mathbf{G}} - \mathbf{K} = \mathbf{F} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

where

$$\mathbf{G} = \frac{m\mathbf{v}}{\sqrt{(1-\beta^2)}}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

$$\mathbf{K} = \frac{2e^2\ddot{\mathbf{v}}}{3c(c^2-v^2)} + \frac{2e^2(\mathbf{v}\ddot{\mathbf{v}})\mathbf{v}}{3c(c^2-v^2)^2} + \frac{2e^2(\mathbf{v}\dot{\mathbf{v}})\dot{\mathbf{v}}}{e(c^2-v^2)^2} + \frac{2e^2(\mathbf{v}\dot{\mathbf{v}})^2\mathbf{v}}{c(c^2-v^2)^3}. \quad (3)$$

G denotes the electromagnetic momentum of the electron in the form due to Lorentz, **K** the reaction due to radiation, *i. e.* the radiation pressure in the form due to Abraham [‡], and **F** the external mechanical force. If we accept the Principle of Relativity for accelerated as well as for uniform

[*] Communicated by the Author.
[†] Schott, 'Electromagnetic Radiation,' pp. 175, 176, 246 (quoted below as E. R.).
[‡] Abraham, *Theorie der Elektrizität*, ii. p. 123.

motion, the expression (2) for the electromagnetic momentum follows as a matter of course, but the expression (3) for the radiation pressure requires a special hypothesis to justify its introduction. It must, however, be borne in mind that the deduction of the Lorentz momentum, as for instance by Planck [*], also implies the existence of a kinetic potential, and that this has only been defined for reversible changes, whilst accelerated motions of an electron involve radiation and therefore are irreversible. If, on the other hand, we adopt the usual equations of the Electron Theory of Larmor and Lorentz together with the hypothesis that the electron occupies a finite though small region of space, whether surface or volume, then the terms on the left of (1) represent merely the first two terms of an infinite series. If a be a length of the same order of magnitude as the linear dimensions of the electron, and l a second length of the order of the radii of curvature and of torsion of its path and of the distance within which its speed is doubled, this series proceeds according to ascending powers of a/l, and converges with sufficient rapidity only when a/l is small compared with $1 - \beta^2$. When the acceleration of the electron becomes very large, or its velocity nearly equal to that of light, the series fails entirely ; indeed it is probable that under these conditions the usual definition of the electromagnetic mass, implied in (2), can no longer be upheld. For the rigid spherical electron of Abraham this has been proved definitely by Sommerfeld [†]; he shows that when the velocity of a uniformly accelerated electron is equal to that of light, the largest term in the mechanical force on it due to its own charge is proportional to the square root of the acceleration when the latter is small. Unfortunately Sommerfeld's method cannot easily be extended to the case of the Lorentz electron, so that it is impossible to be quite sure of what happens here, but it does not seem likely that the result would be very different. However that may be, it is clear that the expressions (1), (2), and (3) must be used with caution in cases where the velocity may be expected to approach that of light, or in very strong electric or magnetic fields, where the acceleration and curvature of the path of the electron may reach large values. Thus we must be careful in using them for an electron which approaches very closely to the nucleus of Rutherford's model atom, and in all problems of a similar kind. May not the failure of the

* Planck, *Sitzungsberichte der Preussischen Akademie der Wissenschaften,* 1907, p. 8.

† "Zur Elektronentheorie," *Göttinger Nachrichten,* 1904, p. 411.

ordinary mechanics and older electrodynamics so often alluded to by present-day investigators of theories of the atom, be after all due to neglect of proper precautions and to unjustifiable usage of confessedly imperfect analytical expressions as much as to defects in the fundamental principles of the electron theory?

2. The equation of energy may be derived from the equation of motion by multiplying it scalarly by the velocity $\mathbf{v}$; after a few simple algebraic transformations it is obtained in the following form * :

$$\dot{\mathrm{T}} - \dot{\mathrm{Q}} + \mathrm{R} = (\mathbf{v}\mathbf{F}), \quad \ldots \ldots \ldots \quad (4)$$

where

$$\mathrm{T} = c^2 m \left\{ \frac{1}{\sqrt{(1-\beta^2)}} - 1 \right\}, \quad \ldots \quad (5)$$

$$\mathrm{Q} = \frac{2ce^2(\mathbf{v}\dot{\mathbf{v}})}{3(c^2 - v^2)^2}, \quad \ldots \ldots \quad (6)$$

$$\mathrm{R} = \frac{2ce^2}{3} \left\{ \frac{\dot{\mathbf{v}}^2}{(c^2 - v^2)^2} + \frac{(\mathbf{v}\dot{\mathbf{v}})^2}{(c^2 - v^2)^3} \right\}. \quad \ldots \quad (7)$$

Here T denotes the kinetic energy of the electron and is given by (5) in the usual form; $(\mathbf{v}\mathbf{F})$ gives the rate of working of the mechanical force; the remaining terms in (4) are derived from the radiation pressure. Of these R is essentially positive and denotes the irreversible rate of loss of energy due to radiation; the expression (7) is the well-known one due to Liénard. On the other hand, $\dot{\mathrm{Q}}$ represents a reversible rate of loss of energy; hence $-\mathrm{Q}$ must be regarded as work stored in the electron in virtue of its acceleration, so that we may speak of it as acceleration energy. Its existence is a direct consequence of a mechanical theory of the æther †.

3. In order to simplify the equations as much as possible it is convenient to introduce a new system of units; we shall choose the

new unit of length $= 2e^2/3c^2m = 1 \cdot 83 \cdot 10^{-13}$ cm.,
,, ,, time $= 2e^2/3c^3m = 6 \cdot 1 \cdot 10^{-24}$ sec.,
,, ,, velocity $= c = 3 \cdot 10^{10}$ cm./sec.,
,, ,, force $= 3c^4m^2/2e^2 = 4 \cdot 3 \cdot 10^6$ dyne,
,, ,, energy $= c^2m = 7 \cdot 88 \cdot 10^{-7}$ erg.

The numerical values given in the last column have been

* E. R. pp. 176, 177.
† E. R. p. 9.

E 2

calculated for the electron with $e = 4 \cdot 65 \cdot 10^{-10}$ E.S.U. and $e/cm = 1 \cdot 77 \cdot 10^7$. When the new units are used we must replace the factor m in (2), $2e^2/3c$ in (3), c^2m in (5), and $2ce^2/3$ in (6) and (7) by unity, the quantity β in (2) and (5) by v, and the velocity c in the expression $c^2 - v^2$ in (3), (6), and (7) by unity.

4. *Introduction of a new time-variable.*—Using the new units we put [*]

$$\tau = \int_0^t \sqrt{(1 - v^2)} \, dt. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

We shall use an accent to denote differentiation with respect to the new time-variable τ, but for the sake of brevity shall use the symbol $\mathbf{w}$ to denote the velocity relative to τ. Then we find in succession

$$\mathbf{v} = \mathbf{w}\sqrt{(1 - v^2)} = \frac{\mathbf{w}}{\sqrt{(1 + w^2)}}, \text{whence} \sqrt{(1 - v^2)} = \frac{1}{\sqrt{(1 + w^2)}},$$

$$\dot{\mathbf{v}} = \frac{\mathbf{w}'}{1 + w^2} - \frac{(\mathbf{w}\mathbf{w}')\mathbf{w}}{(1 + w^2)^2},$$

$$\ddot{\mathbf{v}} = \frac{\mathbf{w}''}{(1 + w^2)^{3/2}} - \frac{(\mathbf{w}\mathbf{w}'')\mathbf{w} + 3(\mathbf{w}\mathbf{w}')\mathbf{w}' + \mathbf{w}'^2\mathbf{w}}{(1 + w^2)^{5/2}} - \frac{4(\mathbf{w}\mathbf{w}')^2\mathbf{w}}{(1 + w^2)^{7/2}}.$$

Substituting these values in the expressions (2), (3), (5), (6), and (7), we find

$$\mathbf{G} = \mathbf{w}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$\mathbf{K} = \frac{\mathbf{w}''}{\sqrt{(1 + w^2)}} - \left\{ \mathbf{w}'^2 - \frac{(\mathbf{w}\mathbf{w}')^2}{1 + w^2} \right\} \frac{\mathbf{w}}{\sqrt{(1 + \mathbf{w}^2)}}, \quad (10)$$

$$\mathbf{T} = \sqrt{(1 + w^2)} - 1, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$\mathbf{Q} = \frac{(\mathbf{w}\mathbf{w}')}{\sqrt{(1 + w^2)}} = \mathbf{T}', \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

$$\mathbf{R} = \mathbf{w}'^2 - \frac{(\mathbf{w}\mathbf{w}')^2}{1 + \mathbf{w}^2} \cdot \cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

With these values the equation of motion (1) becomes

$$\mathbf{w}' - \mathbf{w}'' + \mathbf{R}\mathbf{w} = \mathbf{F}\sqrt{(1 + w^2)}. \quad . \quad . \quad . \quad (14)$$

Similarly the equation of energy (4) becomes

$$\mathbf{T}' - \mathbf{T}'' + \mathbf{R}(\mathbf{T} + 1) = (\mathbf{w}\mathbf{F}). \quad . \quad . \quad . \quad . \quad (15)$$

The curious similarity of form of the last two equations is worthy of remark.

* E. R. p. 292.

Rectilinear Motion.

5. As an example of the use of the equations we have obtained, we shall now consider the case where the electron moves in a straight line under the action of an electrostatic field in the same direction. We shall take the straight line as the axis of x, so that $\mathbf{w}' = w' = x'$. Then we find from (13) and (14) respectively :

$$R = \frac{w'^2}{1+w^2}, \quad \cdots \quad \cdots \quad (16)$$

$$w' - w'' + \frac{ww'^2}{1+w^2} = F\sqrt{(1+w^2)}. \quad \cdots \quad \cdots \quad (17)$$

In order to reduce these equations to a simpler form we write

$w = \sinh\chi$, whence $v = \beta = \tanh\chi$, and $T = \cosh\chi - 1$, (18)
(16) and (17) now give

$$R = \chi'^2, \quad \cdots \quad \cdots \quad \cdots \quad (19)$$

$$\chi' - \chi'' = F. \quad \cdots \quad \cdots \quad \cdots \quad (20)$$

When F is known as a function of τ, (20) may be solved at once in the form

$$\chi = \int_0^\tau F d\tau - \epsilon^\tau \int_0^\tau F\epsilon^{-\tau} d\tau + A + B\epsilon^\tau, \quad \cdots \quad (21)$$

where A and B are arbitrary constants to be determined from the initial conditions. A third arbitrary constant will be introduced when we determine x from the differential equation $x = w = \sinh\chi$, but we may make this constant zero by choosing the origin of coordinates so that x vanishes when t and τ vanish.

6. *Determination of the arbitrary constants A and B.*—One relation can be obtained at once between A and B, for we are at liberty to choose the origin of time so that v, and therefore also χ, vanishes when $\tau = 0$. This condition with (21) gives

$$A + B = \quad , \quad \cdots \quad \cdots \quad (22)$$

Substituting for A in (21) we obtain

$$\chi = \int_0^\tau F d\tau - \epsilon^\tau \int_0^\tau F\epsilon^{-\tau} d\tau + B(\epsilon^\tau - 1). \quad \cdots \quad (23)$$

Bearing in mind our choice of the origins of space and time

and using (8) and (18), we find

$$x = \int_0^\tau \sinh \chi \, d\tau, \quad \ldots \ldots \quad (24)$$

$$t = \int_0^\tau \cosh \chi \, d\tau. \quad \ldots \ldots \quad (25)$$

We have now fully utilized the initial conditions so far as they relate to the initial values of the coordinate and the velocity of the electron, but there still remains an arbitrary element—the arbitrary constant B in (23) to be determined. Here we are brought face to face with one point of difference between the ordinary mechanics of Newton and the electron mechanics founded on the electron theory. Very slight consideration shows that the presence of the third arbitrary constant is due to the fact that the equation of motion of the electron, (1), or (14), or (17), when regarded as a differential equation for the coordinate, is of the third order, and that the differential coefficient of the third order arises from the radiation terms. It is important to bear in mind that these terms must be present whether we adopt the Theory of Relativity for accelerated motions, or base our mechanics on the hypothesis of the extended electron ; only in the latter case every additional term of higher order which we introduce into our equation of motion brings with it another arbitrary constant. These additional arbitrary elements, in so far as they must be determined by the initial conditions, represent the effect on the motion of the electron of its past history, a point which I have emphasized on previous occasions [*]. Unfortunately, the past history is unknown in many problems, and therefore we are compelled to make some additional hypothesis to overcome the difficulty. We must choose it so as to preserve the continuity of the electron mechanics with the ordinary mechanics, which we know suffices in all cases where the velocity of the electron is infinitely small compared with that of light : thus the proper hypothesis suggests itself, namely, that in these cases Newton's Laws of Motion hold without alteration. Hence we assume provisionally :

When the velocity of the electron is zero, its acceleration is equal to the external mechanical force per unit mass.

This hypothesis has the advantage, as we shall see later, that it leads to simple results which can be controlled by experiment.

[*] Schott, *Annalen der Physik*, 1908, p. 63 ; E. R. p. 155.

7. In order to apply the new hypothesis to our problem we must find the acceleration. From (18) together with the expressions given in § 4 we obtain

$$\dot{v} = \frac{w'}{(1+w^2)^2} = \operatorname{sech}^3 \chi \cdot \chi' . \quad . \quad . \quad . \quad (26)$$

Again we find from (23)

$$\chi' = \left\{ \mathrm{B} - \int_0^\tau \mathrm{F} \epsilon^{-\tau} d\tau \right\} \epsilon^\tau . \quad . \quad . \quad . \quad (27)$$

Hence applying our new hypothesis we obtain

$$\mathrm{B} = \chi_0' = \mathrm{F}_0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

where the suffix is used to denote initial values. Substituting this value in (23) ... (25) we get finally

$$\chi = \int_0^\tau \mathrm{F} d\tau - \epsilon^\tau \int_0^\tau \mathrm{F} \epsilon^{-\tau} d\tau + \mathrm{F}_0(\epsilon^\tau - 1), \quad . \quad . \quad . \quad (29)$$

$$x = \int_0^\tau \sinh \left\{ \int_0^\tau \mathrm{F} d\tau - \epsilon^\tau \int_0^\tau \mathrm{F} \epsilon^{-\tau} d\tau + \mathrm{F}_0(\epsilon^\tau - 1) \right\} d\tau, \quad (30)$$

$$t = \int_0^\tau \cosh \left\{ \int_0^\tau \mathrm{F} d\tau - \epsilon^\tau \int_0^\tau \mathrm{F} \epsilon^{-\tau} d\tau + \mathrm{F}_0(\epsilon^\tau - 1) \right\} d\tau. \quad (31)$$

We also find from (19) and (29)

$$\mathrm{R} = \left\{ \mathrm{F}_0 - \int_0^\tau \mathrm{F} \epsilon^{-\tau} d\tau \right\}^2 \epsilon^{2\tau}. \quad . \quad . \quad . \quad . \quad . \quad (32)$$

In order better to appreciate the import of our hypothesis we shall now apply the solutions (29) ... (32) to the particular case of a uniform force.

8. *Example—Motion of a Lorentz electron in a uniform electrostatic field parallel to the line of motion.* I have already treated this example elsewhere [*], but without taking the radiation pressure into account.

In the present problem F is a constant, so that we may omit the zero suffix as no longer necessary. Then we find

$$\chi = \mathrm{F}\tau, \quad \mathrm{F}x = \cosh \chi - 1, \quad \mathrm{F}t = \sinh \chi, \quad \mathrm{R} = \mathrm{F}^2. \quad . \quad (33)$$

Eliminating χ between the second and third of these equations, we obtain precisely the same relation between x and t as we do when we neglect radiation. This surprising result is a direct consequence of the hypothesis of § 6 ; in order to

* E. R. p. 181.

understand this better we must examine the energy relations of the electron.

From (11) we obtain by means of (18) and (33)

$$T = \cosh \chi - 1 = Fx. \quad \cdots \quad (34)$$

This equation shows that the whole of the work done by the external field is converted into kinetic energy of the electron, just as if there had been no radiation at all. None of it is radiated.

Again, from (12) we find by means of (33) and (34)

$$Q = T' = \sinh \chi \cdot \chi' = F^2 t = Rt. \quad \cdots \quad (35)$$

Thus we see that the energy radiated by the electron is derived entirely from its acceleration energy; there is as it were an internal compensation amongst the different parts of the radiation pressure, which causes its resultant effect to vanish.

The total energy radiated is on the present hypothesis only a very small fraction of the kinetic energy, unless the external force be exceptionally large. From (33) ... (35) we find by means of (18)

$$\frac{Rt}{T} = \frac{F \sinh \chi}{\cosh \chi - 1} = F \sqrt{\frac{1 + \sqrt{(1 - v^2)}}{1 - \sqrt{(1 - v^2)}}}. \quad \cdots \quad (36)$$

In applying this equation we must bear in mind that we are using the new units of § 3 ; hence when we return to C.G.S. units we must replace F by $2e^2F/3c^4m^2 = 2e^3X/3c^4m^2$, where X is the electric force in E.S.U. From the value of the new unit of force given in § 3, viz. $4.3 \cdot 10^6$ dyne, and that of e, viz. $4.65 \cdot 10^{-10}$ E.S.U., we find that F in (36) is equal to $1.08 \cdot 10^{-14}$, and that Rt/T is about $4.03 \cdot 10^{-14}$ when X is 30,000 volt/cm. and v or β is 0·5.

9. In order to test the truth of the hypothesis of § 3 we must examine what happens when it fails. Still confining our attention to the case of an electron moving in a uniform electric field along the line of motion, let us return to equations (18) and (23) ... (25), which are true quite independently of the hypothesis in question. Bearing in mind that F as well as B is a constant, we see that we may write instead of (28)

$$B = F(1 + \delta), \quad \cdots \quad (37)$$

where δ is another constant, *i. e.* a quantity independent of χ or v, but generally a function of F. We may regard δ as a measure of the deviation of our hypothesis from the truth.

We now find instead of (33)

$$\chi = F\{\tau + \delta(\epsilon^\tau - 1)\}, \quad R = F^2\{1 + \delta\epsilon\tau\}^2, \quad . \quad . \quad (38)$$

while we have as before

$$v = \beta = \tanh\chi, \quad x = \int_0^\tau \sinh\chi\, d\tau, \quad t = \int_0^\tau \cosh\chi\, d\tau.$$

Changing the independent variable from τ to χ we obtain

$$
\left.
\begin{aligned}
Fx &= \int_0^\chi \frac{\sinh\chi\, d\chi}{1 + \delta\epsilon^\tau} = \int_0^\chi \frac{\sinh\chi\, d\chi}{1 + \delta - \tau + \chi/F}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \\
Ft &= \int_0^\chi \frac{\cosh\chi\, d\chi}{1 + \delta\epsilon^\tau} = \int_0^\chi \frac{\cosh\chi\, d\chi}{1 + \delta - \tau + \chi/F}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \\
R &= F^2\{1 + \delta\epsilon^\tau\}^2 = F^2\{1 + \delta - \tau + \chi/F\}^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \\
\int_0^t R\,dt &= F\int_0^\chi \{1 + \delta\epsilon^\tau\}\cosh\chi\, d\chi = F\int_0^\chi \{1 + \delta - \tau + \chi/F\}\cosh\chi\, d\chi.
\end{aligned}
\right\} \quad (39)
$$

The equations (38) and (39) show that the analytical character of the solution is completely altered by the failure of the hypothesis under consideration; what change will be produced in the numerical results depends on the magnitudes of β, F, and δ. In estimating this change we must bear in mind that what we measure by experiment is the increase of velocity produced in a measured distance by a field of known strength, and perhaps in certain cases the total energy radiated in the process. Knowing β and therefore χ we can calculate x and the energy radiated by means of (39); but in order to measure β independently of the hypothesis to be tested we must not use a deflexion method, either with an electric or a magnetic field, because that would again involve the hypothesis and require very troublesome calculations. We must measure the kinetic energy, *e. g.* by a thermopile, and thence calculate χ and β by means of (18).

When the exponential term in (38) for χ is negligible in comparison with the first, we have the case already considered in § 8; for the sake of brevity we shall speak of it as the Newtonian motion. On the other hand, when the exponential term preponderates we have another extreme case, which we shall call the exponential motion and shall now examine.

10. *The exponential motion.*—We retain only the exponential term in (38), and accordingly only the term χ/F in the expression $1 + \delta - \tau + \chi/F$, which occurs in (39). Then the denominators in the integrals for x and t vanish at the

lower limit, so that t becomes infinite although x remains finite. For this reason it is convenient to extend the integrals from a finite lower limit χ_0 to the upper limit χ_1, the suffixes $_0$ and $_1$ being used to indicate initial and final values respectively. Using the notation of the exponential integral we find from (39)

$$
\left.
\begin{aligned}
x_1 - x_0 &= \int_{\chi_0}^{\chi_1} \frac{\sinh \chi}{\chi} d\chi = \frac{1}{2}\{\mathrm{Ei}(\chi_1) - \mathrm{Ei}(\chi_0) - \mathrm{Ei}(-\chi_1) + \mathrm{Ei}(-\chi_0)\} \\
t_1 - t_0 &= \int_{\chi_0}^{\chi_1} \frac{\cosh \chi}{\chi} d\chi = \frac{1}{2}\{\mathrm{Ei}(\chi_1) - \mathrm{Ei}(\chi_0) + \mathrm{Ei}(-\chi_1) - \mathrm{Ei}(-\chi_0)\} \\
\mathrm{R} = \chi^2, \int_{t_0}^{t_1} \mathrm{R}\,dt &= \chi_1 \sinh \chi_1 - \cosh \chi_1 - \chi_0 \sinh \chi_0 + \cosh \chi_0. \quad . \quad .
\end{aligned}
\right\} \quad (40)
$$

These expressions involve neither F nor δ, but only χ_0 and χ_1, so that in this extreme case of the exponential motion the result depends only on the initial and final velocities of the electron, and not at all on the strength of the field or on the precise value of δ. This fact of itself is sufficient to prove that the exponential motion is not realisable experimentally, at any rate not with the electric fields at our command; a numerical example may make this clearer.

Let us take the case of an electron which has its speed increased by an electric field of 27,700 volt/cm. (giving F equal to 10^{-14}) from $\beta_0 = 0.01$ to $\beta_1 = 0.30$, *i. e.* from $\chi_0 = 0.01$ to $\chi_1 = 0.31$.

With the help of tables of the exponential integral * and of the hyperbolic functions we obtain the following results for the two limiting motions :—

	Newtonian motion.		Exponential motion.	
	Units of § 3.	C.G.S. units.	Units of § 3.	C.G.S. units.
$x_1 - x_0$ ...	$4.8 \cdot 10^{12}$	0.88	0.302	$5.5 \cdot 10^{-14}$
$t_1 - t_0$ ...	$3.05 \cdot 10^{13}$	$1.86 \cdot 10^{-10}$	3.458	$2.1 \cdot 10^{-23}$
$\int_{t_0}^{t_1} \mathrm{R}\,dt$ ...	$3.05 \cdot 10^{-15}$	$2.4 \cdot 10^{-21}$	0.049	$3.9 \cdot 10^{-8}$

A comparison of the numbers in the last four columns of this table shows conclusively the enormous difference between the two limiting motions, and there can be no question that the Newtonian motion is in far better agreement than the exponential motion with what we know from experience. Even if the hypothesis of § 6 be not exactly true, its deviation

* Dale, 'Tables of Mathematical Functions,' p. 85 and p. 64.

from the truth, as measured by the number δ, must be exceedingly small. In order to obtain some idea of its amount we must study the general motion of § 9 a little more fully.

11. *The limits of accuracy of the hypothesis.*—As we have already remarked in § 9, the theoretically best method of testing the hypothesis in question depends upon a comparison of the kinetic energy, T, acquired by the electron with the work, Fx, done by the external field. We see from (18) and (39) that T differs from Fx by a finite amount, the difference being derived from the acceleration energy of the electron. Suppose then that as a result of experiment we find

$$T = \cosh\chi - 1 = (1+f)\mathrm{F}x = (1+f)\mathrm{F}\int_0^\tau \sinh\chi\, dt, \quad (41)$$

where f is a number, which is probably a small fraction with the same sign as δ. We must express δ in terms of f by means of (38), (39), and (41). Let us substitute for χ in (41) its expression in terms of τ and δ given by (38), expand both sides of the equation in ascending powers of F$\delta\epsilon^\tau$ by means of Taylor's theorem and integrate with respect to τ. Rearranging the terms according to powers of F$\delta\epsilon^\tau$ we find

$$\mathrm{F}\delta\,\frac{(1+f\mathrm{F}^2)\epsilon^\tau\sinh \mathrm{F}(\tau-\delta)-(1+f)\mathrm{F}\epsilon^\tau\cosh \mathrm{F}(\tau-\delta)+(1+f)\mathrm{F}(\cosh \mathrm{F}\delta + \mathrm{F}\sinh \mathrm{F}\delta)}{1-\mathrm{F}^2}$$

$$+\mathrm{F}^2\delta^2\,\frac{(4+f\mathrm{F}^2)\epsilon^{2\tau}\cosh \mathrm{F}(\tau-\delta)-2(1+f)\mathrm{F}\epsilon^{2\tau}\sinh \mathrm{F}(\tau-\delta)-(1+f)\mathrm{F}(2\sinh \mathrm{F}\delta + \mathrm{F}\cosh \delta)}{2(4-\mathrm{F}^2)}$$

$$+ \ldots = f\{\cosh \mathrm{F}(\tau-\delta)-1\}-(1+f)\{\cosh \mathrm{F}\delta-1\}. \quad\quad (42)$$

We must combine this equation with (38) so as to eliminate τ and determine δ, but the calculation is so difficult that the result will hardly repay the labour expended; hence we shall content ourselves with finding limits for δ.

We first observe that the series on the left side of (42), being derived from exponential series by integration, is absolutely convergent for all values of F$\delta\epsilon^\tau$, and that the coefficients of all powers of Fδ increase with τ provided that $\tanh \mathrm{F}(\tau-\delta)$ is greater than fF, a condition which is satisfied in actual experiments on account of the smallness of F. Hence the first term on the left, which for such values of τ has the sign of δ, is less than the right-hand member when δ is positive, and of course f also positive, but is

greater (numerically) when δ, and of course f, is negative. Thus when δ is positive, we can obtain an upper limit for its value by omitting all positive terms in the factor of $F\delta$ and all negative ones in the right-hand member of the equation. In this way we find

$$F\delta\epsilon^\tau\{\tanh F(\tau-\delta)-(1+f)F\} < f\{1-\text{sech}\, F(\tau-\delta)\}.$$

This expression can be simplified very considerably without raising the limit appreciably in any actual experiment. In fact we see from (38) that $F(\tau-\delta)$ is less than χ or $\tanh^{-1}\beta$, whence we easily prove that $\text{sech}\, F(\tau-\delta)$ is greater than $\sqrt{(1-\beta^2)}$, and $\tanh F(\tau-\delta)$ greater than $\beta-F\delta\epsilon^\tau$, so that

$$F\delta\epsilon^\tau\{\beta-(1+f)F-F\delta\epsilon^\tau\} < f\{1-\sqrt{(1-\beta^2)}\}.$$

From this equation we find, again making use of (38), that

$$\delta\epsilon^\delta < (\beta/2F)\,\epsilon^{\beta/2F}\left(\frac{1-\beta}{1+\beta}\right)^{1/2F}, \quad \cdot \quad \cdot \quad \cdot \left.\begin{matrix} \\ \\ \end{matrix}\right\}$$

$$\text{provided that} \qquad f < \frac{\{\beta-(1+f)F\}^2}{4\{1-\sqrt{(1-\beta^2)}\}}. \quad \cdot \quad \cdot \quad \right\} \quad \cdot \quad \cdot \quad (43)$$

Of course, as we have stated above, (43) presupposes that δ is positive.

12. Hitherto no experiments appear to have been made in which both the kinetic energy and the work done by the external field have been measured directly as our investigation supposes, but in the course of some determinations of e/m the fall of potential has been measured directly, while the speed of the electron has been determined, usually by means of the deflexion produced by a known magnetic field. The calculation of the speed, and hence of the kinetic energy, from the magnetic deflexion involves an error due to the radiation, presumably of the same order as f but unknown, so that experiments of this kind cannot be expected to supply us with an accurate value of δ. Nevertheless they may be expected to give us some information as to its order of magnitude.

One of the latest determinations of this kind has been made by Hupka [*] for velocities ranging from one quarter to one half of the velocity of light and falls of potential from 4000 to 20,000 volt/cm. measured to within about 1 in 400. Assuming e/m to be $1·77 . 10^7$, Hupka calculated the velocity β from the measured fall of potential by means of the Lorentz formula (18) for the kinetic energy, of course neglecting the effect of radiation which we wish to estimate. In his

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[*] Hupka, *Ann. der Phys.* 1910 (1), p. 169.

experiments he measured the magnetic force required to produce a prescribed radius of curvature in the path of the electron, and compared their product with the ratio $\beta/\sqrt{(1-\beta^2)}$ to which it should be proportional for the Lorentz electron. This proportionality was found to hold throughout the whole range of the measurements to within about 1 in 4000. It is obvious that this constancy of the ratio of the two quantities to be compared could only be possible either if the hypothesis were nearly true, or if in the event of its failure the errors compensated each other exactly. Of course it is extremely improbable that the effect of radiation on the kinetic energy should balance its effect on the magnetic deflexion so as to produce exact compensation, but in the absence of a complete theory of the magnetic deflexion absolute certainty is impossible. We may, however, draw the conclusion that the number f, which measures the difference between the kinetic energy and the work done by the external field, is of the same order of magnitude as the errors in Hupka's experiments. By far the greatest error is that in the determination of the fall of potential, given above as 1 in 400; hence we conclude that f is about $1/400$.

From six experiments with about equal falls of potential we find that the fall of potential used by Hupka for a velocity $\beta = 0\cdot5$ is nearly 20,000 volt/cm., which corresponds to $F = 7\cdot2 \cdot 10^{-15}$. The corresponding upper limit for f given by (43) is $0\cdot47$, which is far beyond the error possible in the experiments; hence we may apply (43). On account of the very small value of F, the last factor of the right-hand member of the first equation is alone effective in determining the order of δ. Taking logarithms of both sides we find

$$\mathrm{Log}_{10}(1/\delta) > 10^{13}. \quad \ldots \quad \ldots \quad (44)$$

13. Let us now consider the case where δ is negative. From (38) we see that $F(\tau-\delta)$ is greater than χ, so that the whole investigation of § 12 applies provided that the sign "less than" be replaced by "greater than." Thus (44) gives a lower limit for $-\delta$.

We may, however, obtain an upper limit for $-\delta$ by a different line of argument, based on the fact that according to (38) χ increases to a maximum as τ increases, and thereafter diminishes again. The maximum is given by $\tau = \log(-1/\delta)$ and is equal to $F\{\log(-1/\delta)-1-\delta\}$, and there is a corresponding maximum value of β, which is $\tanh F\{\log(-1/\delta)-1-\delta\}$. Experiment shows no trace of the existence of such a maximum, so that we may be sure

that if it exists the velocities hitherto found for electrons lie very much below it. If therefore we calculate the value of $(-1/\delta)$ from the highest value of β found for a given value of F, this will certainly give us an upper limit for $-\delta$. In this way we find

$$-\delta\epsilon^{\delta} < \epsilon^{-1}\left(\frac{1-\beta}{1+\beta}\right)^{1/2\mathrm{F}} \quad . \quad . \quad . \quad . \quad (45)$$

With the same experimental data that we have used in § 13 we find

$$\mathrm{Log}_{10}(-1/\delta) > 10^{13},$$

practically the same limit as in the former case.

Hence we may assert as a result of Hupka's experiments that the deviation δ of the hypothesis of § 6 from the truth amounts to less than one part in the ten-million-millionth power of ten for a field of 20,000 volt/cm. This is the same thing as saying that for an electron moving with a velocity small compared with that of light in an electric field of the intensity stated, the acceleration differs from the mechanical force per unit mass by a fraction δ at most, in excess or defect.

It is possible that the deviation δ may depend upon the intensity of the electric field, but the experiments give no certain information on this point. The probable error seems to be rather smaller for a field of 5000 volt/cm. than for the stronger field, but the number of determinations is too small to afford a decisive result. Consequently it would be unsafe to draw any definite conclusion from the experiments respecting the dependence of δ on the field-intensity. Whatever this may be, it does not appear to be very considerable; hence it seems probable that our hypothesis may also be applied to variable fields of intensities of the same order of magnitude as those used in these experiments.

Since according to § 6 the hypothesis is equivalent to Newton's Second Law of Motion for slowly moving electrons, we have verified this law to a degree of accuracy far beyond that attained in astronomical investigations.

How far the law can be applied to electrons starting from rest in very intense fields such as those inside and close to the atom remains doubtful.

VII. *Note on the separation of a Fraction into Partial Fractions.* *By* I. J. Schwatt [*].

THE following method for the separation of a fraction, whose denominator is a power of a linear expression, into partial fractions is simpler than the methods I have given before [†].

To separate into partial fractions

$$F(x) = \frac{\sum\limits_{a=0}^{n} m_a x^{n-a}}{(x+a)^p}.$$

Let $x = y - a$, then

$$F(y-a) = \frac{\sum\limits_{a=0}^{n} m_a (y-a)^{n-a}}{y^p} \quad \ldots \quad (1)$$

or

$$F(y-a) = y^{-p} \sum\limits_{a=0}^{n} m_a \sum\limits_{\beta=0}^{n-a} (-1)^\beta \binom{n-\alpha}{\beta} y^{n-a-\beta} a^\beta. \quad (2)$$

Letting $\alpha + \beta = \gamma$, (2) becomes

$$F(y-a) = \sum\limits_{\alpha=0}^{n} m_a \sum\limits_{\gamma=\alpha}^{n} (-1)^{\gamma-a} \binom{n-\alpha}{\gamma-\alpha} y^{n-p-\gamma} a^{\gamma-a}. \quad (3)$$

Now since

$$\sum\limits_{\alpha=0}^{n} \sum\limits_{\gamma=\alpha}^{n} A\alpha, \gamma = \sum\limits_{\gamma=0}^{n} \sum\limits_{\alpha=0}^{\gamma} A\alpha, \gamma, \quad \ldots \quad (4)$$

therefore

$$F(y-a) = \sum\limits_{\gamma=0}^{n} y^{n-p-\gamma} \sum\limits_{\alpha=0}^{\gamma} (-1)^{\gamma-a} m_a \binom{n-\alpha}{\gamma-\alpha} a^{\gamma-a}. \quad (5)$$

We shall now distinguish between the two cases $n < p$ and $n \geq p$.

(i.) $n < p$.

We may write (5) in the form

$$F(y-a) = \sum\limits_{\gamma=0}^{n} \frac{\sum\limits_{a=0}^{\gamma} (-1)^{\gamma-a} m_a \binom{n-\alpha}{\gamma-\alpha} a^{\gamma-a}}{y^{p-(n-\gamma)}}. \quad (6)$$

Letting $\gamma = n - g$, and $\gamma - \alpha = h$, we have

$$F(y-a) = \sum_{g=0}^{n} \frac{\sum_{h=0}^{n-g}(-1)^h m_{n-g-h}a^h\binom{g+h}{h}}{y^{p-g}}.$$

Therefore

$$F(x) = \sum_{g=0}^{n} \frac{\sum_{h=0}^{n-g}(-1)^h m_{n-g-h}a^{h}\binom{g+h}{h}}{(x+a)^{p-g}} \quad . \quad . \quad . \quad (7)$$

(ii.) $n \geqq p$.

Let $n = p + q$, then (5) becomes

$$F(y-a) = \sum_{\gamma=0}^{p+q} y^{q-\gamma} \sum_{\alpha=0}^{\gamma} (-1)^{\gamma-\alpha} m_a \binom{p+q-\alpha}{\gamma-\alpha} a^{\gamma-\alpha}$$

or

$$F(y-a) = \sum_{\gamma=0}^{q} y^{q-\gamma} \sum_{\alpha=0}^{\gamma} (-1)^{\gamma-\alpha} m_a \binom{p+q-\alpha}{\gamma-\alpha} a^{\gamma-\alpha}$$

$$+ \sum_{\gamma=q+1}^{p+q} \frac{\sum_{\alpha=0}^{\gamma} (-1)^{\gamma-\alpha} m_a \binom{p+q-\alpha}{\gamma-\alpha} a^{\gamma-\alpha}}{y^{\gamma-q}} \quad . \quad . \quad (8)$$

The last result may be changed to

$$F(y-a) = \sum_{\gamma=0}^{q} y^{q-\gamma} \sum_{\alpha=0}^{\gamma} (-1)^{\alpha} a^{\alpha} m_{\gamma-a} \binom{p+q-\gamma+\alpha}{\alpha}$$

$$+ \sum_{\gamma=1}^{p} \frac{\sum_{\alpha=0}^{q+\gamma} (-1)^{q+\gamma-\alpha} m_a \binom{p+q-\alpha}{q+\gamma-\alpha} a^{q+\gamma-\alpha}}{y^{\gamma}}, \quad (9)$$

or

$$F(y-a) = \sum_{\gamma=0}^{q} y^{q-\gamma} \left[\sum_{\alpha=0}^{\gamma} (-1)^{\alpha} a^{\alpha} m_{\gamma-a} \binom{p+q-\gamma+\alpha}{\alpha} \right]$$

$$+ \sum_{\gamma=1}^{p} \frac{\sum_{\alpha=0}^{q+\gamma} (-1)^{\alpha} m_{q+\gamma-a} a^{\alpha} \binom{p+\alpha-\gamma}{\alpha}}{y^{\gamma}} \quad . \quad . \quad (10)$$

Therefore

$$F(x) = \sum_{\gamma=0}^{q} (x+a)^{q-\gamma} \left[\sum_{\alpha=0}^{\gamma} (-1)^{\alpha} a^{\alpha} m_{\gamma-a} \binom{p+q-\gamma+\alpha}{\alpha} \right]$$

$$+ \sum_{\gamma=1}^{p} \frac{\sum_{\alpha=0}^{q+\gamma} (-1)^{\alpha} a^{\alpha} m_{q+\gamma-a} \binom{p+\alpha-\gamma}{\alpha}}{(x+a)^{\gamma}}. \quad . \quad . \quad (11)$$

But

$$\sum_{\gamma=0}^{q} (x+a)^{q-\gamma} = \sum_{\gamma=0}^{q} \sum_{\beta=0}^{q-\gamma} \binom{q-\gamma}{\beta} x^{\beta} a^{q-\gamma-\beta}$$

$$= \sum_{\beta=0}^{q} \sum_{\gamma=0}^{\beta} \binom{q-\gamma}{\beta} x^{\beta} a^{q-\gamma-\beta}.$$

We therefore obtain

$$F(x) = \sum_{\beta=0}^{q} x^{\beta} \sum_{\gamma=0}^{\beta} \binom{q-\gamma}{\beta} a^{q-\gamma-\beta} \left[\sum_{\alpha=0}^{\gamma} (-1)^{\alpha} a^{\alpha} m_{\gamma-\alpha} \binom{p+q+\alpha-\gamma}{\alpha} \right]$$

$$+ \sum_{\gamma=1}^{p} \frac{\sum_{\alpha=0}^{q+\gamma} (-1)^{\alpha} a^{\alpha} m_{q+\gamma-\alpha} \binom{p+\alpha-\gamma}{\alpha}}{(x+a)^{p}}.$$

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VIII. *Note on the Expansion of a Function.*
By I. J. Schwatt [*].

To expand

$$\log^{n}(1+x) \quad \ldots \quad \ldots \quad (1)$$

in powers of x.
We have

$$\log(1+x) = \int_{0}^{x} \frac{dx}{1+x} = \int_{0}^{x} \sum_{\alpha_0=0}^{\infty} (-1)^{\alpha_0} x^{\alpha_0} dx = \sum_{\alpha_0=0}^{\infty} (-1)^{\alpha_0} \frac{x^{\alpha_0+1}}{\alpha_0+1} \ldots \quad (2)$$

Now

$$\log^{2}(1+x) = 2\int_{0}^{x} \log(1+x) \frac{dx}{1+x} = 2\int_{0}^{x} \sum_{\alpha_0=0}^{\infty} (-1)^{\alpha_0} \frac{x^{\alpha_0+1}}{\alpha_0+1} \sum_{\alpha_1=0}^{\infty} (-1)^{\alpha_1} x^{\alpha_1} dx$$

$$= 2\int_{0}^{x} \sum_{\alpha_0=0}^{\infty} \sum_{\alpha_1=0}^{\infty} (-1)^{\alpha_0+\alpha_1} \frac{x^{\alpha_0+\alpha_1+1}}{\alpha_0+1} dx.$$

Letting $\alpha_0 + \alpha_1 = \beta$, then

$$\log^{2}(1+x) = 2\int_{0}^{x} \sum_{\alpha_0=0}^{\infty} \sum_{\beta=\alpha_0}^{\infty} (-1)^{\beta} \frac{x^{\beta+1}}{\alpha_0+1} dx$$

$$= 2 \sum_{\beta=0}^{\infty} \sum_{\alpha_0=0}^{\beta} (-1)^{\beta} \frac{x^{\beta+2}}{(\alpha_0+1)(\beta+2)}.$$

Writing α_0 for β and α_1 for α_0, we obtain

$$\log^{2}(1+x) = 2 \sum_{\alpha_0=0}^{\infty} (-1)^{\alpha_0} \frac{x^{\alpha_0+2}}{\alpha_0+2} \sum_{\alpha_1=0}^{\alpha_0} \frac{1}{\alpha_1+1} \quad \ldots \quad (3)$$

Again

$$\log^3(1+x) = 3\int_0^x \log^2(1+x)\frac{dx}{1+x}$$

$$= 3!\int_0^x \sum_{\alpha_0=0}^{\infty}(-1)^{\alpha_0}\frac{x^{\alpha_0+2}}{\alpha_0+2}\sum_{\alpha_1=0}^{\alpha_0}\frac{1}{\alpha_1+1}\sum_{\alpha_2=0}^{\infty}(-1)^{\alpha_2}x^{\alpha_2}dx$$

$$= 3!\int_0^x \sum_{\alpha_0=0}^{\infty}\sum_{\alpha_2=0}^{\infty}(-1)^{\alpha_0+\alpha_2}\frac{x^{\alpha_0+\alpha_1+2}}{\alpha_0+2}\sum_{\alpha_1=0}^{\alpha_0}\frac{1}{\alpha_1+1}dx.$$

Letting $\alpha_0+\alpha_2=\beta$, we have

$$\log^3(1+x) = 3!\int_0^x \sum_{\alpha_0=0}^{\infty}\sum_{\beta=\alpha_0}^{\infty}(-1)^{\beta}\frac{x^{\beta+2}}{\alpha_0+2}\sum_{\alpha_1=0}^{\alpha_0}\frac{1}{\alpha_1+1}dx$$

$$= 3!\sum_{\beta=0}^{\infty}\sum_{\alpha_0=0}^{\beta}(-1)^{\beta}\frac{x^{\beta+3}}{(\alpha_0+2)(\beta+3)}\sum_{\alpha_1=0}^{\alpha_0}\frac{1}{\alpha_1+1}.$$

Writing α_0 for β, α_1 for α_0, α_2 for α_1, then

$$\log^3(1+x) = 3!\sum_{\alpha_0=0}^{\infty}(-1)^{\alpha_0}\frac{x^{\alpha_0+3}}{\alpha_0+3}\sum_{\alpha_1=0}^{\alpha_0}\frac{1}{\alpha_1+2}\sum_{\alpha_2=0}^{\alpha_1}\frac{1}{\alpha_2+1}$$

$$= 3!\sum_{\alpha_0=0}^{\infty}(-1)^{\alpha_0}\frac{x^{\alpha_0+3}}{\alpha_0+3}\left(\prod_{\beta=1}^{2}\sum_{\alpha_\beta=0}^{\alpha_{\beta-1}}\right)\frac{1}{\alpha_\beta+3-\beta} \cdot \cdot \quad (4)$$

We now assume

$$\log^n(1+x) = n!\sum_{\alpha_0=0}^{\infty}(-1)^{\alpha}\frac{x^{\alpha_0+n}}{\alpha_0+n}\left(\prod_{\beta=1}^{n-1}\sum_{\alpha_\beta=0}^{\alpha_{\beta-1}}\right)\frac{1}{\alpha_\beta+n-\beta}. \quad (5)$$

Then

$$\log^{n+1}(1+x) = (n+1)\int_0^x \log^n(1+x)\frac{dx}{1+x}$$

$$= (n+1)!\int_0^x \sum_{\alpha_0=0}^{\infty}(-1)^{\alpha}_0\frac{x^{\alpha_0+n}}{\alpha_0+n}\left(\prod_{\beta=1}^{n-1}\sum_{\alpha_\beta=0}^{\alpha_{\beta-1}}\right)\frac{1}{\alpha_\beta+n-\beta}\sum_{\gamma=0}^{\infty}(-1)^{\gamma}x^{\gamma}dx$$

$$= (n+1)!\int_0^x \sum_{\alpha_0=0}^{\infty}\sum_{\gamma=0}^{\infty}(-1)^{\alpha_0+\gamma}\frac{x^{\alpha_0+\gamma+n}}{\alpha_0+n}\left(\prod_{\beta=1}^{n-1}\sum_{\alpha_\beta=0}^{\alpha_{\beta-1}}\right)\frac{1}{\alpha_\beta+n-\beta}dx.$$

Letting $\alpha_0+\gamma=\delta$, then

$$\log^{n+1}(1+x) = (n+1)!\int_0^x \sum_{\alpha_0=0}^{\infty}\sum_{\delta=\alpha_0}^{\infty}(-1)^{\delta}\frac{x^{\delta+n}}{\alpha_0+n}\left(\prod_{\beta=1}^{n-1}\sum_{\alpha_\beta=0}^{\alpha_{\beta-1}}\right)\frac{1}{\alpha_\beta+n-\beta}dx$$

$$= (n+1)!\sum_{\delta=0}^{\infty}\sum_{\alpha_0=0}^{\delta}(-1)^{\delta}\frac{x^{\delta+n+1}}{(\alpha_0+n)(\delta+n+1)}\left(\prod_{\beta=1}^{n-1}\sum_{\alpha_\beta=0}^{\alpha_{\beta-1}}\right)\frac{1}{\alpha_\beta+n-\beta}.$$

Writing α_0 for δ, α_1 for α_0, α_2 for α_1, etc., we have

$$\log^{n+1}(1+x) = (n+1)! \sum_{\alpha_0=0}^{\infty} (-1)^{\alpha_0} \frac{x^{\alpha_0+n+1}}{\alpha_0+n+1} \sum_{\alpha_1=0}^{\alpha_0} \frac{1}{\alpha_1+n} \left(\prod_{\beta=2}^{n} \sum_{\alpha_\beta=0}^{\alpha_\beta-1} \right) \frac{1}{\alpha_\beta+n+1-\beta}.$$

Or

$$\log^{n+1}(1+x) = (n+1)! \sum_{\alpha_0=0}^{\infty} (-1)^{\alpha_0} \frac{x^{\alpha_0+n+1}}{\alpha_0+n+1} \left(\prod_{\beta=1}^{n} \sum_{\alpha_\beta=0}^{\alpha_\beta-1} \right) \frac{1}{\alpha_\beta+n+1-\beta}, \quad . \quad (6)$$

which proves the correctness of the assumed result (4).

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IX. *On the Collapse of Tubes by External Pressure.*—III.
By R. V. Southwell, *M.A., Fellow of Trinity College,
Cambridge* [*].

IN an interesting paper recently communicated to this
magazine [†], Mr. Cook has dealt with the resistance
offered to external pressure by *short* steel tubes—that is to
say, by tubes such that an appreciable part of their strength
was due to the sealing plugs which in the experiments were
employed to preserve their cylindrical form at the ends.
The subject is one which possesses practical as well as
theoretical interest, since his results, and those of other
workers on the same lines, are foundations upon which we
may endeavour to base scientific rules for the spacing of
" collapse rings " in boiler-flues.

I propose in the present paper to consider the bearing of
these results in regard to design. It appears to me that a
discussion of the problem from this standpoint is becoming
urgently necessary, since the large amount of scientific interest
aroused by it in recent years [‡] has resulted in a steadily
increasing number of formulæ, based either upon analytical
investigations or upon isolated series of experiments, and
tending, by reason of their variety, merely to bewilder
anyone who has not made an extensive study of the subject.

In the first place, however, I desire to remove a slight
difficulty which may be encountered if Mr. Cook's paper is

read in conjunction with my theoretical discussions of earlier date *. This relates to the quantity termed the " critical length," of which Mr. Cook's definition differs slightly from my own.

Both theory and experiment suggest that the length of a tube sensibly affects its resistance to external pressure only in the case of comparatively short tubes, and the earliest definitions of the term " critical length," given almost simultaneously by Profs. A. E. H. Love †—as " the least length for which collapse is possible under the critical pressure "— and A. P. Carman ‡—as a " minimum length, beyond which the resistance of a tube to collapse is independent of the length,"—were in recognition of this fact. Prof. Carman concluded further, from the early experiments of Fairbairn § and from others which he had himself conducted, that " the collapsing pressure varies inversely as the length, for lengths less than the critical length "∥. That is to say, the curve suggested by him as expressing the experimental relation between collapsing pressure and length, for a tube of given thickness and diameter, consists of two discontinuous branches —a straight line, representing constant collapsing pressure, for all lengths above the critical length, and a rectangular hyperbola intersecting this line at a point corresponding to the critical length.

If these views are adopted, the critical length for any definite size of tube may be determined from experiments, by estimating (1) the straight line, parallel to the axis of length, which best represents the collapsing pressure for tubes of considerable length, and (2) the hyperbola which agrees best with the results for the shorter tubes; their point of intersection gives the required value. This is substantially the procedure adopted by Mr. Cook, who finds that within the range of his experiments the critical length L, thus defined, is given satisfactorily by the formula

$$L = 1 \cdot 73 \sqrt{\frac{d^3}{t}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

being the thickness and d the diameter of the tube.

* Phil. Trans. Roy. Soc. A. vol. ccxiii. pp. 187–244 (1913) ; Phil. Mag. September 1913.

† ' Mathematical Theory of Elasticity,' (2nd edition, 1906) p. 530.

‡ University of Illinois Bulletin, vol. iii. No. 17 (June 1906).

§ Phil. Trans. Roy. Soc. vol. cxlviii. p. 389 (1858).

∥ Carman, *loc. cit.* p. 7.

By calculation, I had previously obtained the formula

$$L = \kappa \sqrt{\frac{d^3}{t}}, \quad \ldots \quad \ldots \quad (2)$$

κ being some constant, depending upon the type of the end constraints, of which I have not been able, except in certain ideal cases, to obtain an exact value by analysis [*]; but, as I have already stated, my definition of the critical length is different from Mr. Cook's. I had concluded, as a result of my analysis, that tubes of length such that the strengthening effect of the ends is *sensible, but small*, will collapse under a pressure given by

$$\mathfrak{P} = \frac{t}{d} \left[\alpha \frac{d^4}{l^4} + \beta \frac{t^2}{d^2} \right], \quad \ldots \quad \ldots \quad (3)$$

l being the length of the tube, and α and β constants for any given material [†]. Clearly, as l is increased the collapsing pressure given by this equation falls rapidly, and becomes sensibly equal to $\beta t^3/d^3$. Hence, adopting a slightly modified form of Professor Love's definition, I took the critical length to be "the least length for which collapse is possible under [*a pressure sensibly equal to*] the critical pressure." L being thus defined, and δ some small number which we agree to regard as negligible, we have

$$\alpha \frac{d^4}{L^4} + \beta \frac{t^2}{d^2} = (1 + \delta) \beta \frac{t^2}{d^2},$$

or

$$\alpha \frac{d^4}{L^4} = \beta \delta \frac{t^2}{d^2},$$

whence equation (2) may be derived, κ being equal to $\sqrt[4]{\alpha/\beta\delta}$.

No hyperbolic relation between collapsing pressure and length occurs in the exact analytical treatment of our problem. But the convenience of a relation of this form, and its satisfactory agreement with experiment, suggest that an hyperbola might with advantage be substituted for the discontinuous curve which represents the exact theoretical expression for the collapsing pressure. A curve of this type is illustrated by the thick lines in fig. 3 (which may be regarded as connecting pressure and length) of my paper in the Philosophical Magazine for May 1913: it is composed

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[*] Phil. Trans. Roy. Soc. A. vol. ccxiii. p. 227 (1913).
[†] *Cf.* my equation (1), Phil. Mag. September 1913, p. 503.

of a series of intersecting arcs, of which those shown in the figure (as I pointed out in the same paper *) are very approximately enveloped by a rectangular hyperbola.

The curves of which these arcs are fragments are those members of the family represented by the equation

$$\mathbb{P} = 2\mathrm{E}\frac{t}{d}\left[\frac{Z}{k^4(k^2-1)}\frac{d^4}{l^4} + \frac{1}{3}\frac{m^2}{m^2-1}(k^2-1)\frac{t^2}{d^2}\right], \quad (4)$$

in which k has positive integral values. k denotes the number of lobes characterizing the cross-section of the tube after collapse, and of the other quantities appearing in (4), besides those which have already been defined—

E is Young's modulus, and

$\dfrac{1}{m}$ is Poisson's ratio, for the material of the tube;

Z is a constant, depending upon the type of the end-constraints†.

Now it is easy to show that the curve represented by (4) is touched by the rectangular hyperbola

$$\mathbb{P} = \frac{8}{3}\mathrm{E}\frac{t^2}{ld}\frac{1}{k}\sqrt[4]{\frac{Z}{9}\left(\frac{m^2}{m^2-1}\right)^3\frac{t^2}{d^2}(k^2-1)^2}, \quad (5)$$

at a point given by

$$l = \frac{d}{k}\sqrt[4]{9\frac{m^2-1}{m^2}\frac{Z}{(k^2-1)^2}\frac{d^2}{t^2}}, \quad (6)$$

and the occurrence of k in (5) shows that the family of curves (4) is not exactly enveloped by any one hyperbola. But the hyperbola touching that member of the family for which $k=3$ gives values for the collapsing pressure which are in satisfactory agreement with those obtainable from the exact (discontinuous) curve, and which err on the side of safety throughout the practically important range of lengths. We may therefore take the equation to this hyperbola, viz.

$$\mathbb{P} = \frac{32}{9}\mathrm{E}\frac{t^2}{ld}\sqrt[4]{\frac{Z}{36}\left(\frac{m^2}{m^2-1}\right)^3\frac{t^2}{d^2}}, \quad (7)$$

as representing the collapsing pressure of short tubes, and Prof. Bryan's formula ‡

$$\mathbb{P} = 2\frac{m^2}{m^2-1}\mathrm{E}\frac{t^3}{d^3} \quad \quad (8)$$

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* p. 698.
† *Cf.* Phil. Mag. September 1913, p. 503.
‡ Phil. Mag. September 1913, p. 504.

for those cases in which it gives a higher value for p than we should obtain from (7).

The theoretical value of the "critical length," as Prof. Carman and Mr. Cook have defined the term, is then given by the point of intersection of (7) and (8). We find

$$L = \frac{16}{9} \sqrt[4]{\frac{Z}{36} \frac{m^2 - 1}{m^2} \frac{a^6}{t^2}}, \quad \cdots \quad (9)$$

which agrees in form with Mr. Cook's equation (1). The latter equation is therefore supported by my analysis, although the "critical length" with which it deals is a quantity differing from that which was considered by me in my earlier papers.

The significance of the foregoing investigation lies in the fact that the expression for the critical length given by (9) is almost entirely independent of the material composing the tube. In so far as it varies with the elastic constants,

$$L \propto \sqrt[4]{1 - \frac{1}{m^2}}, \quad \cdots \quad (10)$$

and the value of the quantity on the right of (10) ranges from 0·985 in the case of glass (for which $1/m = 0·258$) to 0·951 in the case of copper (for which $1/m = 0·428$)*. *It is highly probable, therefore, that Mr. Cook's equation (1) has an application much wider than the range of his experiments.*

The point is, I think, worth investigation in future experimental work. If Mr. Cook's equation should be found to be thus generally applicable, it will introduce important simplifications into the problem of design. For a knowledge of the critical length and of a formula giving the minimum collapsing pressure for a tube of given thickness, diameter, and material is, as I shall now attempt to show, sufficient for all practical purposes.

At the present time there is no generally accepted formula for the collapsing pressure of long tubes. The results of theory are naturally unreliable in practice, since the perfectly elastic and homogeneous tube which it presupposes is an ideal not practically realizable : those of experiment have the disadvantage of restricted scope and, further, give relations between the collapsing pressure and the ratio of thickness to diameter which are not expressible in any simple formula. I have tried to show † that these experimental relations can

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* The authorities for these figures are given by Love, *op. cit.* p. 103; the figures given above represent an extreme range of values.

† Phil. Mag. September 1913.

be *explained*; but what is needed in practice is a simple and comprehensive formula, *involving constants which can be determined for any given material from one or two of the ordinary tests, without the employment of elaborate tube-testing apparatus*; and I do not know of any formula hitherto published which satisfies these conditions.

The theoretical formula for long tubes has been given in equation (8) of this paper. In form it has been found satisfactory as a representation of experimental results for *thin* tubes: the experimental constant given by Carman for steel tubes is some 25 per cent. less than the theoretical value [*], but this reduction may be explained as due in part to unavoidable inaccuracies in his experimental tubes and in part to his employment of rather too large a range of experiments (his formula is known to give excessive values for the collapsing pressures of his thicker tubes) in the determination of the constant.

In endeavouring to explain the complete failure of the theoretical formula (8) to give the collapsing pressures of fairly thick tubes, I have emphasized [†] the important part which elastic breakdown plays in accelerating collapse. It would seem, indeed, that we must not expect any long tube to withstand a pressure which is more than sufficient to impair its elastic properties. Thus, if y_c is the stress corresponding to the yield-point of a material in compression, we ought to base our design upon the hypothesis that a tube of this material will certainly collapse under a pressure given by [‡]

$$\mathbb{P} = 2\frac{t}{d}y_c. \quad . \quad . \quad . \quad . \quad . \quad (11)$$

For tubes of less than a certain limiting thickness the formula (8) gives a smaller value of the collapsing pressure than this, collapse being possible, owing to the occurrence of elastic instability, under a pressure which is not sufficient to impair the elasticity of the tube, so long as it remains circular. What we want, then, is an expression for $\mathbb{P}$ which is practically equivalent to (8) in the case of very thin tubes and which in no case exceeds the value given by (11).

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[*] Cook (*loc. cit.* p. 52) estimates the reduction as 30 per cent., but I think this figure is somewhat excessive; my estimate is based on the figures E = 30,500,000, $1/m = 0.3$.

[†] Phil. Mag. September 1913.

[‡] Equation (11) tacitly assumes that the compressive stress is uniformly distributed over an axial section of the tube-wall. Though inaccurate in the case of very thick or short tubes, this assumption is substantially correct for all tubes of practical dimensions.

A simple expression fulfilling these requirements is

$$p = 2\frac{t}{d}\frac{y_c}{1+\dfrac{y_c}{E}\dfrac{d^2}{t^2}}. \quad . \quad . \quad . \quad . \quad (12)$$

As the thickness is reduced, it approaches the limiting value $2E\,t^3/d^3$, which is slightly less than that of Bryan's formula (8); and since the ratio d/t cannot be less than unity, its value is in all cases appreciably less than that which is given by (11). Hence, provided that a tube is accurate in form and of uniform material, it is clear that the pressure given by this equation would be insufficient either to collapse it or to impair its elasticity, so that the only modification required for purposes of design is the insertion of a factor of safety which shall make proper allowance for practical imperfections. Since the equation as it stands gives an estimate of the collapsing pressure which errs on the side of safety, I believe that 2 would be amply sufficient as a factor of safety; but this point can be investigated by a comparison with the experimental results hitherto obtained.

The similarity of (12) with the Rankine-Gordon formula for columns will be at once remarked. Dr. Lilly * was the first to recommend the employment of an equation of this form, but in place of y_c and E he suggests the insertion of constants which are to be determined empirically from the results of a complete series of tube-collapsing tests. In general, when the comparison can be made, I imagine that the difference between his formula and my own will be negligible; but the latter seems to me preferable, first, in that it expressly provides against overstrain of the tube, and secondly, owing to its greater scope : the appropriate factor of safety may be determined from experiments on tubes of any material, and when the corresponding formula for any other material is required, it will be necessary only to change the values of y_c and E, which are quantities determinable from one simple test †.

It may be remarked here that in the case of the lap-welded Bessemer steel tubes tested by Prof. Stewart ‡, the average value of the stress at the yield-point was stated to be 37,000 pounds per square inch. If we assume a value of 30,000,000 pounds per square inch for the modulus of elasticity (which

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* Trans. Inst. Civ. Eng. Ireland, vol. xxxvi. pp. 138-164 (1910).
† For practical purposes it will be sufficiently accurate to substitute y_t, the yield-point in tension, for y_c; and an ordinary tensile test is therefore all that is necessary.
‡ Trans. American Soc. Mech. Eng., vol. xxvii. pp. 730-822 (1905-6).

does not appear to have been determined), equation (12) will give, as the collapsing pressure of these tubes,

$$\mathfrak{P} = \frac{74{,}000}{\dfrac{d}{t} + \dfrac{1}{810}\dfrac{d^3}{t^3}} . \quad \cdots \quad \cdots \quad (13)$$

Dr. Lilly * has given the formula

$$\mathfrak{P} = \frac{80{,}000}{\dfrac{d}{t} + \dfrac{1}{1000}\dfrac{d^3}{t^3}} \quad \cdots \quad \cdots \quad (14)$$

as very closely representing the results of this series of experiments. Thus (13), which could be written down without reference to any experiments besides that required to find the yield-point and Young's modulus, gives values which closely agree with those actually obtained from hydraulic tests, and which (as may be shown by drawing a line to represent (13) in fig. 3 of Dr. Lilly's paper) err almost invariably on the side of safety.

It remains to discuss the bearing of Mr. Cook's results upon the problem of spacing " collapse rings." At a first glance equation (1) may appear paradoxical : for if, as has sometimes been assumed, collapse rings ought to be spaced at distances equal to some multiple of the critical length, the thinnest tubes will receive practically no re-inforcement, whilst the thickest must be fitted with rings at quite short intervals. This manifestly unsound result is due to the inaccuracy of the assumption noticed above ; for the function of collapse rings is to strengthen a tube against collapse by instability, and the ratio in which the resistance is required to be increased (which, on the theory adopted by Mr. Cook †, will be equal to the ratio of the critical length to the distance between collapse rings) is obviously greater in the case of the thinnest tubes.

At the same time, considerations of safety suggest that collapse rings ought not to be placed too close together ; for a point may be reached at which failure, if it occurs at all, will involve rupture of the tube-wall close to the rings ‡,—an occurrence which has far more serious consequences than the simple flattening of long tubes at collapse.

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* *Loc. cit.* p. 145.
† Namely, that the collapsing pressure is inversely as the length, for tubes below the critical length.
‡ In the author's experience the walls of quite short tubes, which fail at high pressures, were almost invariably sheared through at collapse.

The best procedure would seem to be to arrange the spacing of collapse rings in such a way that the resistance of thin tubes is brought up to the value given by (11): they will thus be enabled to withstand any pressure which is insufficient to cause elastic breakdown, and a greater pressure than this is in any case inadvisable.

If we take the collapsing pressure for a tube of critical length as given by the equation

$$\mathfrak{P} = 2\mathrm{E}\frac{t^3}{d^3} \quad \ldots \quad \ldots \quad (15)$$

(which, as compared with (8), errs slightly on the side of safety), and employ Mr. Cook's equation (1) for the critical length, the collapsing pressure for a tube in which the collapse rings are spaced at distances s will be given by the equation

$$\left. \begin{aligned} \mathfrak{P} &= \frac{\mathrm{L}}{s} \times 2\mathrm{E}\frac{t^3}{d^3} \\ &= 3\cdot46\frac{\mathrm{E}}{s}\sqrt{\frac{t^5}{d^3}} \end{aligned} \right\} \quad \ldots \quad \ldots \quad (16)$$

Then if the resistance is brought up to the value given by (11) we have

$$2\frac{t}{d}y_c = 3\cdot46\frac{\mathrm{E}}{s}\sqrt{\frac{t^5}{d^3}},$$

or

$$\frac{s}{d} = 1\cdot73\frac{\mathrm{E}}{y_c}\sqrt{\frac{t^3}{d^3}}, \quad \ldots \quad \ldots \quad (17)$$

so that when collapse rings are to be employed we may use (11) to determine the value of t/d, and fix the rings at intervals given by (17).

Now the strengthening effects of collapse rings will be *nil* if $s > \mathrm{L}$: hence, by (1) and (17), their employment is advantageous only when the dimensions given by (12) are such that

$$\frac{t}{d} < \sqrt{\frac{y_c}{\mathrm{E}}}. \quad \ldots \quad \ldots \quad (18)$$

It may be remarked that this result will hold whatever be the value of κ in (2), provided only that the latter equation is correct in *form*. Mr. Cook's experiments suggest that it is. Taking for example the figures given by Prof. Stewart, we find from (18) that collapse rings are of no advantage on a tube of which the diameter is less than 28 times the thickness.

Substituting from (18) in (12), we find, as an alternative form of the result, that collapse rings are useless when the collapsing pressure exceeds a limit given by the equation

$$\mathfrak{P} = \sqrt{\frac{y_c^3}{E}} \cdot \quad . \quad . \quad . \quad . \quad . \quad (19)$$

This limit being of the order 1300 per square inch, the equation suggests that collapse rings may be advantageously employed in all boiler work. But questions other than that of strength may dictate dimensions in practice, and hence (18) is a more convenient form of the result.

Summary.

The paper consists of a review, written from the practical standpoint, of recent theoretical and experimental work on the subject of tube collapse. As a conclusion, the following rules for design are suggested :—

1. Work in terms of a " collapsing pressure " $\mathfrak{P}$, connected with the (specified) working pressure p by the equation

$$\mathfrak{P} = f \cdot p, \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where f is the factor of safety, for which (it is suggested) a value as low as 2 will be sufficient.

2. *When collapse rings are not to be used*, fix the proportions of the tube by means of the formula

$$\mathfrak{P} = 2 \frac{t}{d} \frac{y_c}{1 + \dfrac{y_c}{E} \dfrac{d^2}{t^2}} \cdot \quad . \quad . \quad . \quad (12) \, bis$$

3. *When collapse rings are to be used*, fix the proportions of the tube by the formula

$$\mathfrak{P} = 2 \frac{t}{d} y_c \quad . \quad . \quad . \quad . \quad (11) \, bis$$

(making allowance for corrosion, &c., in cases where the thickness suggested by this formula seems insufficient), and use rigid collapse rings spaced at *equal* * intervals s, given

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* I am indebted to Mr. Cook for suggesting the importance of *equal* spacing, as a means of realizing the experimental conditions of " encastred " ends when Adamson's flanged joints are employed. Such joints tend to keep the tube *circular*, but their influence on the *slope* of the tube-wall is a somewhat doubtful quantity. Mr. Cook points out, however, that with equal spacing of the rings, each section of the flue will be kept *cylindrical* at the ends, just as the ends of each span are virtually " encastred " when a long continuous beam, uniformly loaded, is supported by several equidistant piers.

by the equation

$$\frac{s}{d} = 1 \cdot 73 \frac{\mathrm{E}}{y_c} \sqrt{\frac{t^3}{d^3}}. \quad \cdots \quad (17) \; bis$$

4. Collapse rings can be advantageously employed when, and only when, the dimensions of a tube are such that

$$\frac{t}{d} < \sqrt{\frac{y_c}{\mathrm{E}}}. \quad \cdots \quad (18) \; bis$$

In the equations (11), (12), (17) and (18), t denotes the thickness and d the diameter of the tube : these quantities, and s, must be expressed in terms of the same units; y_c is the stress at the yield-point in compression (for practical purposes the yield-point in tension may be substituted), and E is Young's modulus for the material of the tube : these quantities, and P, must be expressed in terms of the same units.

For additional security, it would perhaps be advisable to substitute 1·5 for the factor 1·73, equation (17) having been based on an estimate (15) for the collapsing pressure of long tubes which is somewhat in excess of Carman's. Moreover, the figure 1·73 is based solely upon equation (1), and, as Mr. Cook has remarked *, his tests cannot be regarded as sufficient in number or covering a great enough range of dimensions to confirm this equation definitely.

August 21, 1914.

X. *A Summary of Einstein and Grossmann's Theory of Gravitation.* By Dr. A. D. FOKKER (*Leiden*) †.

1. PERHAPS it might be useful to give a brief account of the principal features of Einstein and Grossmann's gravitation theory ‡, leaving aside as far as possible the mathematical complications, but emphasizing the simple and fundamental physical points.

Unfortunately, this theory will be of little direct importance to experimental physics. Not because it fails to indicate any experiments which could bring evidence for its validity or non-validity, but because the foreseen effects probably are far too small to be detected by present experimental methods.

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* *Loc. cit.* p. 56.
† Communicated by Prof. W. H. Bragg, F.R.S.
‡ *Entwurf einer Verallgemeinerten Relativitätstheorie und einer Theorie der Gravitation*, Phys. Teil v. A. Einstein, Math. Teil v. M. Grossmann, 1913 (Teubner). A. Einstein, *Phys. Zeitschr.* xiv. p. 1251 (1913).

The largest effect occurs in the case of the bending of light-rays in a strong gravitational field. The strongest field available is the sun's. A light-ray passing near the sun's surface should suffer a bending through an angle of 0·83 seconds of arc, so that the position of a star when the sun is nearly touching it should be shifted away from the sun's centre. Perhaps the next eclipse may reveal such an effect[*]. Another consequence of the theory is the influence of the gravitation potential on the rate of action of physical processes. For example, the vibrations in the atoms should be slower at the sun's surface than on the earth. As a matter of fact, there has been observed a general shift of solar spectral lines to the red side of the spectrum as compared with lines from terrestrial sources [†], but the solar conditions are so complicated that no definite conclusion can yet be drawn from this.

2. Notwithstanding the fact that the theory cannot give much hope for new discoveries in experimental physics, it cannot be said to be chiefly a mathematical speculation. For throughout its development the lines followed are lines of physical thought, and Einstein's intuition has only trusted truly physical principles. The reason why these had to be so few is that a century of experimenting has failed to bring to light an appreciable influence of gravitation on other phenomena.

Indeed, when the theory of relativity had concluded that gravitation was to be propagated with the speed of light [‡], it was difficult to look for an extension of Newton's theory, which henceforth had to be considered as a first approximation, without any new experimental indications as to the direction in which this extension was to be sought. There seemed to be too much freedom, the number of possible assumptions seemed not to be restricted enough to point in any definite direction.

Einstein considers of fundamental importance the fact that all bodies fall with the same acceleration ; combined with the assumption of the identity of gravitating and inertial mass, it led him to work out the consequences of his ' Aequi-valenz-Hypothese,' which will be described further on.

Next he bases himself on the principle of the conservation

* War has made this impossible.
† Compare E. Freundlich, *Phys. Zeitschr.* xv. p. 369 (1914).
‡ For the consistency of this propagation with astronomical observations *cp.* H. A. Lorentz, Proc. R. Ac. Sc. Amsterdam, viii. p. 603 (1900) ; H. A. Lorentz, *Phys. Zeitschr.* xi. (1910).

of energy, which seems to be a sufficiently trustworthy basis, and admits that the principle of relativity shall be valid in a particular case, that is, its formulæ will be correct whenever the gravitation potentials are constants independent of the coordinates. To be complete, we state explicitly that it is believed that the results of experiments in a laboratory are not altered when the laboratory, as a whole, is taken to a place where the gravitation potentials have other values.

Starting from these ideas, Einstein has been able to give the laws according to which matter is affected by a gravitation field, and a gravitation field created by matter. It is of special interest that his theory is not constructed after the known model of the electromagnetic theory (though we find certain analogies to be present). He places the phenomena of gravitation on a higher plane, and accordingly shows how the equations of the electromagnetic field are to be altered when allowance must be made for the presence of a gravitation field.

It is characteristic of his theory, that the field of gravitation is not given by a single potential, but by a set of ten potentials, functions of the coordinates *. These ten potentials are the components of a symmetrical tensor. Further, the important thing which is acted upon by gravitation and which produces the field, formerly the " mass " alone, is in the present theory a tensor of stresses, momenta, currents of energy, and energy. This will be made clearer afterwards†.

The Equivalence Hypothesis.

3. The equivalence hypothesis briefly assumes the equivalence of a homogeneous field of gravitation and a uniform acceleration of the system of coordinates.

Consider the case, that an experimenter is working in a room without any window, so that he cannot know anything about things outside, and does not know whether he is in relative motion against an outside world or not. Let the only remarkable thing he notices be this, that all bodies fall down to the floor when he lets them loose, all with the same acceleration, in the same direction. Shall he be able to state whether his room is in a homogeneous gravitation field or whether there is no gravitation field at all, the cause of falling down and apparent weight of his bodies being a uniformly accelerated motion of his room through space?

He cannot. He has no criterion. Of course, if all bodies did not fall with the same acceleration, there would be no

* See § 11.   † See § 12.

reason to admit the possibility of his room being accelerated. There would be no reason to suspect that there was anything the matter with his room, affecting all bodies in the same way. Again, there could be no reason for doubt, if he could find an inertial mass which did not gravitate. Yet, as far as the experiments of Eötvös have gone [*], they seem to confirm that bodies which are attracted by the earth with the same force have equal inertial masses as measured by the centrifugal forces excited by their motion in the earth's daily rotation.

It is clear, that when we consider the motions of bodies, using the ordinary mechanics, no distinction can be made between a homogeneous gravitation field and a uniformly accelerated system of coordinates.

4. We may put the equivalence hypothesis in another form. If we know the laws of motion in a field without gravitation, we know the differential equations connecting the time and the coordinates referred to a certain system of coordinates. We are not obliged to describe the motion with reference to this system. If we choose to do so, we may describe the motion with reference to another system which relatively to the first is uniformly accelerated. Of course we shall have then to introduce alterations in our equations.

The equivalence hypothesis states that the alterations to be introduced are the same as those which we have to make when there is a homogeneous gravitation field affecting the motion.

It extends this statement beyond the region of mechanics. It assumes that for all physical phenomena, when we give the laws referred to an accelerated system of coordinates, the differential equations will undergo the same variations from what they were in the resting systems as they would suffer if we produced a gravitation field.

5. Starting from this idea, it is easy to deduce in an elementary manner some important consequences [†].

For example, consider two sodium atoms, placed one above the other at a certain distance h, and fixed on the Z-axis of a system of coordinates that has a constant acceleration (γ) upwards. Let at some instant a signal, consisting of a train of wavelets, be sent from the upper sodium atom to the

* B. Eötvös, *Mathem. u. naturwissensch. Berichte aus Ungarn.* vii. 1890. Wiedemann, *Beiblätter,* xv. p. 688 (1891).

† A. Einstein, *Annalen der Physik,* xxxv. p. 898 (1911).

lower. To cover the distance h a certain time is required, say $\dfrac{h}{c}$ as a first approximation, when c denotes the velocity of light. Then the velocity v_0 of the upper atom at the moment of sending the signal is less than the velocity $v_0 + \gamma\dfrac{h}{c}$ of the lower atom, when the signal arrives there. Thus the wavelets on arrival, according to Doppler's principle, will appear to have a wave-length which is $\left(1 + \dfrac{\gamma h}{c^2}\right)$ times shorter. According to the equivalence hypothesis, the same would be observed if the sodium atoms were at rest in a system where a homogeneous gravitation field existed having a gradient $\dfrac{\partial \phi}{\partial z} = \gamma$. This means that a vibrating sodium atom, compared with another that is placed in a spot where the potential is less by an amount $\Delta\phi$, would seem to vibrate $\left(1 + \dfrac{\Delta\phi}{c^2}\right)$ times as fast as the latter. Thus, an observed terrestrial sodium line ought to be shifted to the violet, when compared with a solar sodium line.

Again, let a beam of light be sent at a certain moment by a horizontal collimator at a point $x = a$, $y = 0$, $z = b$ of the moving system towards the axis of Z. To cover the distance a, a certain time is required. When the beam of light is observed by a telescope fixed to the Z-axis, this telescope will in the meanwhile have acquired an upward velocity $v_0 + \dfrac{a\gamma}{c}$, if v_0 is the velocity of the collimator at the moment of sending the beam. According to the common aberration theory, the telescope will have to be directed a little upward to observe the beam. In the accelerated system the light-rays will apparently be curved lines. By hypothesis, the same is to be the case in a homogeneous gravitation field. In order to account for this apparent rotation of the wave fronts we must, following Huyghens's principle, conclude that the velocity of light is greater in upper regions, where the gravitation potential is higher.

Of course these considerations are only approximate, but they bring out important conclusions of the theory.

<center>The transformation from a resting into an accelerated
system of coordinates.</center>

6. The equations which relate the coordinates and the time, ξ, η, ζ, and τ, of the resting system to the coordinates

and time, x, y, z, t, of the moving system must now be indicated more exactly. In deducing them use is made of the postulate, that the velocity of light at each point of the moving system should be independent of the direction of the light-beam, and therefore a function of the coordinates only. In our case, where we shall suppose the system (x, y, z, t) accelerated along the axis of Z, the velocity is a function of z only. Lorentz * gave the equations in the exact form

$$\left.\begin{aligned} \xi &= x, \quad \eta = y, \\ \zeta &= a(z - z_0), \\ c\tau &= b(z - z_0), \end{aligned}\right\} \quad \cdots \quad \cdots \quad (a)$$

where c is a constant, the velocity of light in the resting system, and

$$a = \tfrac{1}{2}(e^{kt} + e^{-kt}), \quad b = \tfrac{1}{2}(e^{kt} - e^{-kt}).$$

The constant k is connected with the (variable) velocity of light, c', in the points of the moving system by the relation

$$c' = k(z - z_0).$$

The approximate equations given by Einstein † and valid for very small values of t, so that t^3 may be neglected, are easily deduced from these. They are

$$\left.\begin{aligned} \xi &= x, \quad \eta = y, \\ c\tau &= c't, \\ \zeta &= (1 + \tfrac{1}{2}k^2t^2)(z - z_0) = z - z_0 + \frac{1}{2}\frac{c'^2t^2}{z - z_0}. \end{aligned}\right\} \quad \cdot \quad (b)$$

From the last equation we see

$$\zeta = z - z_0 + \frac{1}{2}\frac{c^2\tau^2}{z - z_0},$$

that at $\tau = 0$ the starting acceleration of the different points of the system is given by $g_0 = \dfrac{c^2}{z - z_0}$. Speaking exactly, the acceleration is not the same for the different points of the system. Nor is it the same throughout the time. A perfectly constant acceleration, by the way, would lead to a contradiction with the old relativity theory, because it would lead to an infinite velocity. We can see more distinctly

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* H. A. Lorentz, *Het Relativiteitsbeginsel.* Drie voordrachten, bewerkt door Dr. W. H. Keesom, 1913 (De Erven Loosjes, Haarlem).

† A. Einstein, *Annalen der Physik*, xxxviii. pp. 359, 444 (1912).

what the acceleration will be if, availing ourselves of the relation $a^2 - b^2 = 1$, we notice from (a) that

$$\zeta^2 - c^2\tau^2 = (z - z_0)^2, \quad \zeta = \sqrt{(z - z_0)^2 + c^2\tau^2},$$

and, therefore, for a point with a fixed value of z,

$$\frac{d\zeta}{d\tau} = \frac{c^2\tau}{\sqrt{(z - z_0)^2 + c^2\tau^2}},$$

so that the velocity of the moving system will never exceed the velocity of light. From this follows for the acceleration

$$g = \frac{d^2\zeta}{d\tau^2} = \frac{c^2(z - z_0)^2}{\sqrt{(z - z_0)^2 + c^2\tau^2}^3}.$$

This gives for $\tau = 0$ the starting acceleration g_0 as found above. The constant k has no particular meaning. It relates the value of the velocity of light as measured in the moving system to the velocity of light in the other. If g_{00} be the acceleration of the origin $z = 0$ at the time $t = 0$, and we want our system of coordinates defined in such a manner that at this same point and time the velocity of light c'_{00} be the same as in the resting system, then we have to take $k = \dfrac{g_{00}}{c}$. For we see easily that $z_0 = -\dfrac{c^2}{g_{00}}$, and if $c'_{00} = -kz_0$ is to be equal to c, then we must have $k = g_{00}/c$, as stated.

Lastly, we may notice that to the differential equations

$$d\zeta = a\,dz + bc'dt, \quad c\,d\tau = ac'dt + b\,dz$$

correspond, by virtue of $a^2 - b^2 = 1$, the reciprocal equations

$$dz = a\,d\zeta - bc\,a\tau, \quad c'dt = ac\,d\tau - b\,d\zeta.$$

Motion of a free particle.

7. Now, knowing the motion of a free point through a space without gravitation (and such is the motion in our resting system) to be in a straight line, Einstein, by using the relation of the coordinates of the two systems, could find the equations of motion when referred to the moving axes. He found it possible * to contract them into the form of Hamilton's principle :

$$\delta\left\{\int H'dt\right\} = 0,$$

* *Ann. d. Phys.* xxxviii. p. 458 (1912).

in which H′ was to be put

$$\mathrm{H}' = -m\sqrt{c'^2 - v^2},$$

v being the point's velocity with components $\dfrac{dx}{dt}, \dfrac{dy}{dt}, \dfrac{dz}{dt}$, and m its mass.

There is a striking resemblance between this form and the form in which the equations of motion may be given in a space without gravitation. It is known that according to the principle of relativity in that case the function H must be written

$$\mathrm{H} = -m\sqrt{c^2 - \left(\frac{d\xi}{d\tau}\right)^2 - \left(\frac{d\eta}{d\tau}\right)^2 - \left(\frac{d\zeta}{d\tau}\right)^2},$$

and that Hamilton's principle in that case is

$$\delta\left\{\int \mathrm{H}\, d\tau\right\} = 0.$$

If we define as the *length of the four-dimensional line-element* determined by $d\xi, d\eta, d\zeta, d\tau$,

$$ds = \sqrt{c^2\, d\tau^2 - d\xi^2 - d\eta^2 - d\zeta^2},$$

we may, omitting the constant factor $-m$, put

$$\delta\left\{\int ds\right\} = 0,$$

which means that the moving particle between two points of its path traces the shortest line possible through the four-dimensional space.

If we try to express the line-element ds in the differentials of the new coordinates, we find, as a matter of fact, that

$$ds = \sqrt{c^2\, d\tau^2 - d\xi^2 - d\eta^2 - d\zeta^2} = \sqrt{c'^2\, dt^2 - dx^2 - dy^2 - dz^2}.$$

Thus we see that $\delta\left\{\int ds\right\} = 0$ expresses equally well our equation $\delta\left\{\int \mathrm{H}'\, dt\right\} = 0$, and that the free particle, which in the system of (x, y, z, t) is a *free falling* particle, still moves along the shortest line possible through four-dimensional space, if ds again defines the length of the line-element given by dx, dy, dz, dt. The length of an element ds appears thus as a quantity not altered by a transformation of coordinates.

The only quantity in the equation which is a function of the coordinates, and therefore might and does play the rôle of a gravitation potential, is the quantity c'^2, and we see that it is nothing but one of the coefficients determining the length of ds in terms of dx, dy, dz, dt.

It is very satisfactory that the equation of motion is now put in a form which is not affected by our transformation of coordinates. The statement that a free particle always takes the shortest possible track between two points of four-dimensional space is very simple, and reminds one of the principle, put forward by Hertz in his *Prinzipïen der Mechanik*, that a free system ¦moves along the straightest line possible.

The Gravitational Potentials $g_{\mu\nu}$.

8. The next step is to consider Hamilton's principle in the form

$$\delta\left\{\int ds\right\} = 0,$$

to be valid still farther beyond the present case. It holds in the old theories, and it holds after the special transformation of the coordinates which is equivalent to a certain fairly homogeneous gravitation field. We will now assume that it will hold also after an arbitrary transformation of co-ordinates, which will be equivalent to an arbitrary unhomo-geneous field.

Now, when we execute an arbitrary transformation

$$\xi = f_1(x, y, z, t),$$
$$\eta = f_2(x, y, z, t),$$
$$\zeta = f_3(x, y, z, t),$$
$$\tau = f_4(x, y, z, t),$$

then, of course, substituting in ds^2 for the differentials $d\xi$, $d\eta$, $d\zeta$, $d\tau$ their expressions in dx, dy, dz, dt, the line-element will be expressed by a form

$$ds^2 = g_{11}dx^2 + 2g_{12}dx\,dy + 2g_{13}dx\,dz + 2g_{14}dx\,dt \left.\begin{matrix} \\ \\ \\ \\ \end{matrix}\right\}$$
$$+\ g_{22}dy^2\ \ + 2g_{23}dy\,dz + 2g_{24}dy\,dt$$
$$+\ g_{33}dz^2\ \ + 2g_{34}dz\,dt \qquad (1)$$
$$+\ g_{44}dt^2,$$

in which there are *ten* coefficients $g_{\mu\nu}$, in general all of them functions of the coordinates. In the equation of motion these ten functions will give the influence of the gravitation field on the motion of a particle.

Thus it appears that in the theory there will be henceforth a set of *ten gravitation potentials*.

In the particular case of the fairly homogeneous field we

considered this set degenerated in a set of four :

$$g_{11}=g_{22}=g_{33}=-1, \; g_{44}=c'^2, \; (g_{12}=g_{13}=g_{14}=g_{23}=g_{24}=g_{34}=0),$$

of which only $g_{44}=c'^2$ was a variable function of the co-ordinates. In the absence of a gravitation field even this potential becomes a constant.

If we write the fundamental equation

$$\delta\{\textstyle\int ds\} = 0, \quad \ldots \ldots \quad (2)$$

in the form of Hamilton's principle,

$$\delta\{ \textstyle\int \mathrm{H}' dt \} = 0,$$

by putting

$$\mathrm{H}' = -m\frac{ds}{dt},$$

then we know that this equation is equivalent to

$$\frac{d}{dt}\left(\frac{\partial \mathrm{H}'}{\partial \dot{x}}\right) - \frac{\partial \mathrm{H}'}{\partial x} = 0.$$

It is through the ten potentials $g_{\mu\nu}$ that H' depends on the coordinates.

Laws of Conservation.

9. In order to show how phenomena are affected by gravitation, and the gravitational field is created by matter, and how the laws of conservation of energy and momentum are preserved in the theory, we shall have to use tensors. To introduce them it will be best to show how the laws of conservation can be expressed for a special case in electro-dynamics, and in absence of a gravitational field.

Let $\mathbf{d}$ and $\mathbf{h}$ denote the electric and magnetic vectors in free space. We may conceive stresses X_x, X_y, X_z, &c., existing in the electromagnetic field, and also an electro-magnetic momentum I_x, I_y, I_z per unit volume. If X_x denotes the pressure per unit area exerted on the field at the positive Y side of a surface perpendicular to the axis of X by the field at the negative side of this surface, and if X_y denotes the force per unit area in the direction of X exerted through a surface perpendicular to the field at the negative side of it on the field at the positive side, and if X_z denotes the same with regard to a surface perpendicular to the Z-axis, then the X-component of the total force upon an element $dx\,dy\,dz$ is

$$-\left(\frac{\partial \mathrm{X}_x}{\partial x} + \frac{\partial \mathrm{X}_y}{\partial y} + \frac{\partial \mathrm{X}_z}{\partial z}\right) dx\,dy\,dz,$$

and this must be the increase of the momentum present in the element, if the law of conservation of momentum is to be fulfilled. Thus we see that this law is expressed by the equation :

$$\frac{\partial X_x}{\partial x} + \frac{\partial X_y}{\partial y} + \frac{\partial X_z}{\partial z} + \frac{\partial T^x}{\partial t} = 0.$$

Similarly, if S_x, S_y, S_z, and E denote the currents of energy in the field and the energy per unit volume, the law of conservation of energy is expressed by the equation :

$$\frac{\partial S_x}{\partial x} + \frac{\partial S_y}{\partial y} + \frac{\partial S_z}{\partial z} + \frac{\partial E}{\partial t} = 0.$$

Now, introducing the symmetrical coordinates

$$x_1 = x, \quad x_2 = y, \quad x_3 = z, \quad x_4 = ict,$$

and writing $L_{\sigma\nu}(\sigma = 1, 2, 3, 4, \nu = 1, 2, 3, 4)$ for our stresses, momenta, and energy, so that

$$
\begin{array}{cccc}
L_{11} & L_{12} & L_{13} & L_{14} \\
L_{21} & L_{22} & L_{23} & L_{24} \\
L_{31} & L_{32} & L_{33} & L_{34} \\
L_{41} & L_{42} & L_{43} & L_{44}
\end{array}
=
\begin{array}{cccc}
X_x & X_y & X_z & icI_x \\
Y_x & Y_y & Y_z & icI_y \\
Z_x & Z_y & Z_z & icI_z \\
\dfrac{i}{c}S_x & \dfrac{i}{c}S_y & \dfrac{i}{c}S_z & -E,
\end{array}
$$

we see that these equations have all the same form,

$$\frac{\partial L_{11}}{\partial x_1} + \frac{\partial L_{12}}{\partial x_2} + \frac{\partial L_{13}}{\partial x_3} + \frac{\partial L_{14}}{\partial x_4} = 0,$$

and that the laws of conservation of energy and momentum can be concentrated in one formula :

$$\sum_\nu \frac{\partial L_{\sigma\nu}}{\partial x_\nu} = 0.$$

If we express the quantities $L_{\sigma\nu}$ in terms of the components of **d** and **h** according to the formulæ of Maxwell, Poynting, and Abraham, we see that the set of the functions $L_{\sigma\nu}$ form a symmetrical square. Here they are :

$$
\begin{array}{cccc}
\frac{1}{2}\{d^2 - 2d_x^2 + h^2 - 2h_x^2\}, & -d_x d_y - h_x h_y, & -d_x d_z - h_x h_z, & i(d_y h_z - d_z h_y), \\
-d_y d_x - h_y h_x, & \frac{1}{2}\{d^2 - 2d_y^2 + h^2 - 2h_y^2\}, & -d_y d_z - h_y h_z, & i(d_z h_x - d_x h_z), \\
-d_z d_x - h_z h_x, & -d_z d_y - h_z h_y, & \frac{1}{2}\{d^2 - 2d_z^2 + h^2 - 2h_z^2\}, & i(d_x h_y - d_y h_x), \\
i(d_y h_z - d_z h_y), & i(d_z h_x - d_x h_z), & i(d_x h_y - d_y h_x), & -\frac{1}{2}(d^2 + h^2).
\end{array}
$$

When there are external forces acting upon the field through the electrons, the laws of conservation are no longer fulfilled for the field alone, the equations are to be replaced by four other ones, contracted into

$$\sum_{\nu} \frac{\partial L_{\sigma\nu}}{\partial x_{\nu}} = F_{\sigma},$$

where F_{σ} denotes the force from the charge upon the field,

$$F_1 = -\rho\left(d_x + \frac{1}{c}\left[v_y h_z - v_z h_y\right]\right),$$

and the work done upon the field

$$F_4 = -\rho\frac{i}{c}(v_x d_x + v_y d_y + v_z d_z),$$

these being equal and opposite to the force of the field upon the charge.

But F_{σ} being the force exerted by material agents upon the field, there must be an equal loss of momentum and energy of these agents per unit time. Denoting by $M_{\sigma\nu}$ the stresses, momenta, currents, and energy in the matter, the laws of conservation demand that

$$F_{\sigma} = -\sum_{\nu} \frac{\partial M_{\sigma\nu}}{\partial x_{\nu}}.$$

Thus, finally, the laws of conservation are now expressed by

$$\sum_{\nu} \frac{\partial(L_{\sigma\nu} + M_{\sigma\nu})}{\partial x_{\nu}} = 0.$$

Tensors.

10. A set of sixteen quantities such as $L_{\sigma\nu}$ is called a tensor of the second order. It is a fundamental property of a tensor that when a transformation of coordinates is executed the components $L_{\sigma\nu}$ of the tensor transform themselves like $dx_{\sigma}\, dx_{\nu}$. For instance, when we transform our coordinates in the following manner

$$x_1 = p_{11}x_1' + v_{12}x_2' + p_{13}x_3' + p_{14}x_4',$$
$$x_2 = p_{12}x_1' + p_{22}x_2' + p_{23}x_3' + p_{24}x_4',$$
$$x_3 = p_{13}x_1' + p_{23}x_2' + p_{33}x_3' + p_{34}x_4',$$
$$x_4 = p_{14}x_1' + p_{24}x_2' + p_{34}x_3' + p_{44}x_4',$$

then a tensor as a "*geometrical quantity*" is mathematically

defined as a set of quantities $L_{\sigma\nu}$ which transform themselves like

$$L_{\sigma\nu} = \sum_{\substack{\alpha=1\dots4 \\ \beta=1\dots4}} p_{\sigma\alpha} p_{\nu\beta} \, L'_{\alpha\beta}.$$

We can convince ourselves of the fact that $L_{\sigma\nu}$ is transformed as $dx_\sigma \, dx_\nu$ either by direct calculation or by remarking that the stresses, &c. in the electromagnetic field have the same dimensions as stresses, &c. in matter, *f. e.* in a (viscous) gas. When the distribution law of velocities (ξ, η, ζ) is $f(\xi, \eta, \zeta) \, d\xi \, d\eta \, d\zeta$, so that in a space dS there are $f \, d\xi \, d\eta \, d\zeta \, dS$ molecules with the given velocity, then for X_x, the amount of momentum carried across unit of an area perpendicular to the axis of X, we find

$$X_x = \int f \, d\xi \, d\eta \, d\zeta \, \frac{m}{\sqrt{c^2 - v^2}} \cdot \frac{dx}{dt} \cdot \frac{dx}{dt},$$

Similarly, for X_y

$$X_y = \int f \, d\xi \, d\eta \, d\zeta \frac{m}{\sqrt{c^2 - v^2}} \cdot \frac{dx}{dt} \cdot \frac{dy}{dt},$$

and so on.

We see the products $dx \, dx$, $dx \, dy$, that is $dx_\sigma \, dx_\nu$, come in, and entering into details we could prove that indeed the components of a tensor of stresses, momenta, and energy transform themselves as $dx_\sigma \, dx_\nu$.

This property is of great use when we wish to write equations in a form that is invariant against transformations. It causes the four quantities

$$\sum_\nu \frac{\partial L_{\sigma\nu}}{\partial x_\nu} \quad (\sigma = 1, 2, 3, 4)$$

to transform themselves as dx_σ, that is, they are the components of a four-dimensional vector (which might be called a tensor of the first order). Therefore, when they are equated to the components of a vector, such as the force (F_σ), then both members of the equations

$$\sum_\nu \frac{\partial L_{\sigma\nu}}{\partial x_\nu} = F_\sigma$$

are transformed in the same way, and the equation persists in the same form:

$$\sum_\beta \frac{\partial L'_{\alpha\beta}}{\partial x'_\beta} = F_\alpha'.$$

11. As long as we deal only with the linear orthogonal transformations of the principle of relativity, the properties of tensors are relatively simple. But our aim is to consider, and we did already consider quite general transformations $x_i = f_i(x_1', x_2', x_3', x_4')$, so that in the transformation formulæ for the differentials

$$dx_\imath = \sum_\kappa p_{\imath\kappa} \, dx_\kappa',$$

the coefficients $p_{\imath\kappa}$ are not such as to make the transformation a linear orthogonal one. Therefore the coefficients $\pi_{\imath\kappa}$ in the reciprocal equations

$$dx_\kappa' = \sum_\imath \pi_{\imath\kappa} \, dx_\imath$$

are not the same functions of the coordinates as $p_{\imath\kappa}$, and we must now distinguish between different kinds of tensors of the second order, namely, *covariant* tensors which transform themselves by the formula

$$\mathrm{T}'_{\mu\nu} = \sum_{\alpha\beta} p_{\alpha\mu} \, p_{\beta\nu} \, \mathrm{T}_{\alpha\beta},$$

contravariant tensors, for which

$$\Theta'_{\mu\nu} = \sum_{\alpha\beta} \pi_{\alpha\mu} \, \pi_{\beta\nu} \, \Theta_{\alpha\beta},$$

and *mixed* tensors, which follow the rule

$$\mathbf{T}'_{\mu\nu} = \sum p_{\alpha\mu} \, \pi_{\beta\nu} \, \mathbf{T}_{\alpha\beta}.$$

For instance, the quantities $g_{\mu\nu}$ which define our invariable line element

$$ds^2 = \sum_{\mu\nu} g_{\mu\nu} dx_\mu \, dx_\nu$$

form a covariant tensor :

$$
\begin{array}{cccc}
g_{11} & g_{12} & g_{13} & g_{14} \\
g_{21} & g_{22} & g_{23} & g_{24} \\
g_{31} & g_{32} & g_{33} & g_{34} \\
g_{41} & g_{42} & g_{43} & g_{44}
\end{array}
\qquad (g_{\mu\nu} = g_{\nu\mu}).
$$

On the contrary, if $\gamma_{\mu\nu}$ is the minor of $g_{\mu\nu}$ in the determinant, divided by the determinant itself, then the tensor of the $\boldsymbol{\gamma}_{\mu\nu}$,

$$
\begin{array}{cccc}
\gamma_{11} & \gamma_{12} & \gamma_{13} & \gamma_{14} \\
\gamma_{21} & \gamma_{22} & \gamma_{23} & \gamma_{24} \\
\gamma_{31} & \gamma_{32} & \gamma_{33} & \gamma_{34} \\
\gamma_{41} & \gamma_{42} & \gamma_{43} & \gamma_{44},
\end{array}
$$

is a contravariant tensor.

Each of both *tensors* can be taken as a *representation of the gravitational field.*

Action of Gravitation on Matter.

12. The tensor $(\mathbf{T}_{\sigma\nu})$ which is closely connected with the stresses, momenta, and energy is a mixed tensor.

Of course, when a gravitation field acts upon matter (let us include an electromagnetic field in the term matter) it cannot be expected that the laws of conservation of momentum and energy will hold for matter in itself alone. Obviously the gravitational field can impart energy and momentum to the material system. In fact, the form $\sum_{\nu} \dfrac{\partial}{\partial x_{\nu}} \mathrm{T}_{\sigma\nu}$ does not vanish now. Einstein gives for the influence of gravitation on other phenomena the formula

$$\sum_{\nu} \frac{\partial \mathbf{T}_{\sigma\nu}}{\partial x_{\nu}} = \frac{1}{2} \sum_{\mu\nu\tau} \frac{\partial g_{\mu\nu}}{\partial x_{\sigma}} \gamma_{\mu\tau} \mathbf{T}_{\tau\nu}. \quad \cdots \quad (3)$$

We notice that the terms which on the right-hand side of the equation determine to what extent a given field will influence the physical phenomena, are precisely the components of the tensor of stresses and energy. This was alluded to in section 2.

As soon as matter and gravitation field are considered together, then of course the laws of conservation must be fulfilled. The existence must be supposed of a tensor of stresses, momenta, and energy in the gravitational field itself. Its components will be functions of the potentials $g_{\mu\nu}$ or $\gamma_{\mu\nu}$ and their derivatives, and, when this tensor is denoted by $\mathbf{t}_{\sigma\nu}$, we shall demand that the laws are expressed by the equations

$$\sum_{\nu} \frac{\partial \mathbf{T}_{\sigma\nu}}{\partial x_{\nu}} + \sum_{\nu} \frac{\partial \mathbf{t}_{\sigma\nu}}{\partial x_{\nu}} = 0.$$

Differential equations for the creation of a gravitational field by matter.

13. This demand, this application of the laws of conservation, has been a guide in investigating the form of the differential equations by which the gravitational field is determined. There must be ten of them, because we have ten potentials. Of course they are to be expected to be extensions of the known equation of Poisson:

$$\Delta \phi = k\rho,$$

where ρ is the density of the attracting mass, and ϕ the

potential. We expect that our differential equation will be

$$\mathbf{G}_{\sigma\nu} = \kappa \mathbf{T}_{\sigma\nu},$$

where $\mathbf{G}_{\sigma\nu}$ denotes a tensor derived by differential operations from our potentials, containing differential coefficients up to those of the second degree. It has in special cases and with certain simplifying neglections to become the same as $\Delta\phi$.

Now, when we put $\mathbf{T}_{\tau\nu} = \mathbf{G}_{\sigma\nu}/\kappa$ in the right-hand side of the first equation of the previous section, we ought, as the second equation indicates, to be able to show that the right-hand side is identical with a sum of differential coefficients.

Indeed, Einstein has succeeded in doing this. He finds that the identity exists if we put

$$\kappa \mathbf{T}_{\sigma\nu} = \sum_{\alpha\beta\mu} \frac{\partial}{\partial x_\alpha} \left(\sqrt{-g} \; \gamma_{\alpha\beta} \, g_{\sigma\mu} \, \frac{\partial \gamma_{\mu\nu}}{\partial x_\beta} \right)$$
$$+ \frac{1}{2} \sqrt{-g} \left(\sum_{\beta\tau\rho} \gamma_{\beta\nu} \frac{\partial g_{\tau\rho}}{\partial x_\sigma} \cdot \frac{\partial \gamma_{\tau\rho}}{\partial x_\beta} - \frac{1}{2} \sum_{\alpha\beta\tau\rho} \delta_{\sigma\nu} \gamma_{\alpha\beta} \frac{\partial g_{\tau\rho}}{\partial x_\alpha} \frac{\partial \gamma_{\tau\rho}}{\partial x_\rho} \right).$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \cdots \quad (4)$$

Here g denotes the determinant of the $g_{\mu\nu}$ and $\delta_{\sigma\nu}$ a quantity which equals 0 for $\sigma \neq \nu$ and 1 for $\sigma = \nu$.

It appears that the differential coefficients $\dfrac{\partial \mathbf{t}_{\sigma\nu}}{\partial x_\nu}$ in the identity are the differential coefficients of the tensor

$$\mathbf{t}_{\sigma\nu} = -\frac{1}{2\kappa} \sqrt{-g} \left(\sum_{\beta\tau\rho} \gamma_{\beta\nu} \frac{\partial g_{\tau\rho}}{\partial x_\sigma} \cdot \frac{\partial \gamma_{\tau\rho}}{\partial x_\beta} - \frac{1}{2} \sum_{\alpha\beta\tau\rho} \delta_{\sigma\nu} \gamma_{\alpha\beta} \frac{\partial g_{\tau\rho}}{\partial x_\alpha} \cdot \frac{\partial \gamma_{\tau\rho}}{\partial x_\beta} \right),$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \cdots \quad (5)$$

so that the stresses, momenta, and energy of the gravitation field are to be taken as given by this formula.

A very important result is seen when we compare this formula with the preceding. It then appears that

$$\kappa(\mathbf{T}_{\sigma\nu} + \mathbf{t}_{\sigma\nu}) = \sum_{\alpha\beta\mu} \frac{\partial}{\partial x_\alpha} \left(\sqrt{-g} \; \gamma_{\alpha\beta} g_{\sigma\mu} \frac{\partial \gamma_{\mu\nu}}{\partial x_\beta} \right), \qquad (6)$$

i. e. the tensor of stresses, &c. of the gravitation field enters exactly in the same way into the differential equations determining the potentials as the material tensor does. The *gravitational stresses, momenta*, and *energy exert the same power in creating the field* as the material ones do. This is quite satisfactory. There is no reason why the energy &c. of the field would behave otherwise than energy of matter.

As already said, the given differential equation fits in with the formula

$$\sum \frac{\partial (\mathbf{T}_{\sigma\nu} + \mathbf{t}_{\sigma\nu})}{\partial x_\nu} = 0, \quad \ldots \quad (7)$$

showing that the laws of conservation are fulfilled.

Approximative simplifications.

14. The differential equations for gravitation appear to be very complicated. However, there is a way of simplifying the equations and getting successive approximations. It has already been said that in the case of constant potentials, let us now say in absence of a gravitation field, the fundamental tensor of the $g_{\mu\nu}$ becomes

$$
\begin{array}{cccc}
-1 & 0 & 0 & 0 \\
0 & -1 & 0 & 0 \\
0 & 0 & -1 & 0 \\
0 & 0 & 0 & c^2,
\end{array}
$$

and accordingly the tensor of the $\gamma_{\mu\nu}$

$$
\begin{array}{cccc}
-1 & 0 & 0 & 0 \\
0 & -1 & 0 & 0 \\
0 & 0 & -1 & 0 \\
0 & 0 & 0 & \dfrac{1}{c^2}.
\end{array}
$$

The first thing we can do is to assume that in the actual case of our solar system the values of $g_{\mu\nu}$ and $\gamma_{\mu\nu}$ will differ only slightly from those given above by very small quantities $g^{*}_{\mu\nu}$ and $\gamma^{*}_{\mu\nu}$, and that, therefore, as a first approximation, we can omit in the differential equations those terms containing products of two $g^{*}_{\mu\nu}$ or $\gamma^{*}_{\mu\nu}$ or their derivatives.

When, besides, we abstract from the actual existing motions, assuming that the velocities are so small as to make $\dfrac{v}{c}$ and $\dfrac{v^2}{c^2}$ negligible, then the equation of Poisson for g^{*}_{44} is the only one retained, and we get Newton's theory, where g^{*}_{44} plays the rôle of the usual gravitation potential. Considering the significance of $g_{44} = c^2 + g^{*}_{44}$ in the form for the line-element ds, the conclusions may be drawn about the dependency of the velocity of light and of the rate of action of processes on the gravitation potentials which we mentioned before (§ 5).

Relativity of Inertia.

15. When we take into account terms with $\frac{v}{c}$, then equations of motion may be derived for a moving particle which furnish us with some remarkable conclusions as to the relativity of inertia.

It was pointed out long ago by Mach[*] that we cannot speak of mass in an absolute sense. Just as we can only speak of the motions, velocities, and accelerations of a body relative to other existing bodies, so we only come to consider the inertiæ of different bodies when we study their mutual action. Mach concluded that we are not justified in thinking of the mass as of something absolute belonging to a particle, but that it may be due to some inducing influence of bodies one upon the other.

If this is true we should expect first, that the inertia of a particle is increased by heaping up other masses in its neighbourhood, and secondly, that an accelerated mass induces an acceleration of the same direction in other masses. For if two masses are accelerated together (amidst other bodies) their mutual acceleration is zero, and the resistance against the mutual acceleration, which is the inertia that they mutually induce one in the other, ought not to come into play. So that when A and B are accelerated together the force required to give A this acceleration is less than it was when B remained at rest. This is the same as saying that the acceleration of B actually gives rise to an accelerating force in A.

It is remarkable that these conclusions follow as *consequences* from Einstein's theory. Indeed, by bringing the other masses nearer, the inertia of a particle is expected to increase, and a sudden acceleration of neighbouring masses would cause an acceleration of the particle.

Unhappily, the amount of the expected effects is so small that there is scarcely any hope of discovering them.

Concluding Remarks.

16. In the absence of experimental evidence, certain points may be laid stress upon which distinguish Einstein's theory from other theories, and give it high intrinsic merits.

It is an advantage that the theory regards the velocity of light no more as an absolute constant. There was something unsatisfactory in the unexplained existence of a certain constant critical velocity.

---

[*] 'Prinzipien der Mechanik in ihrer historischen Entwicklung dargestellt.'

Of fundamental importance is the conclusion of the theory as to the relativity of inertia. Our classical conception of inertia dates from Galilei, and can be said to be derived from the observed behaviour of bodies acting upon one another. But the underlying tacit assumption was that the bodies would behave just the same if they were an isolated system, and cut off from the remaining part of the universe. This is corrected by the theory of Einstein, which makes an influence of this remaining part of the universe responsible for the inertial properties of single systems.

Still more essentially in favour of the theory are the following considerations, which really form the very nucleus of all conceptions of relativity.

In order to describe physical phenomena we must construct systems of coordinates, space-coordinates, and a time-coordinate. With reference to these systems we can express physical relations by certain equations. Now there are two possibilities. Either the equations exist only with reference to certain specialized systems of coordinates, or they exist independent of our choice of coordinates, and retain their form after an arbitrary transformation of coordinates *. In the first case the equation can be suspected to owe its existence to a special artifice of choosing the coordinates, and not to correspond to a real relation. In the second case the equation can only owe its existence to a real relation existing in the nature of things.

That the real relations in nature, and the equation expressing them, are to be independent of any choice of coordinates whatever, is the principle of relativity in its purest and most general form.

This principle was in the older theory of relativity limited to those systems of coordinates connected by the linear orthogonal transformations for which the Euclidean four-dimensional element $d\tau^2 = dx_1^2 + dx_2^2 + dx_3^2 + dx_4^2$ was an invariant. The *Verallgemeinerte Relativitätstheorie* tries to apply the principle in its full extent for all transformations which leave the non-Euclidean general form $ds^2 = \Sigma g_{\mu\nu}\, dx_\mu\, dx_\nu$ invariant. It is for being able to express the laws in their covariant forms that the complicate "absolute differential calculus" with its tensors is worked out.

In fact, the fundamental equations (2) and (3) preserve their form unchanged whatever transformation of coordinates is executed. So do equations (5) and (6). The same cannot be said of the equations (4) and (7). These preserve their form only when the transformation is a linear one. The

* A. Einstein, *Phys. Zeitschr.* xv. p. 176, Feb. 1914.

reason for this lack of generality is the condition that the laws of conservation should be fulfilled. This limits the free choice of coordinates and specializes the admissible systems. It is, however, to be expected that to these differential equations there will correspond other general equations, which preserve their forms for more general transformations. Einstein and Grossmann have found these equations in March 1914, in the form of a variation principle analogous to Hamilton's principle. Indeed, Hamilton's principle is more general than the principle of conservation of energy. Their results have been published in the *Zeitschrift für Mathematik und Physik*, lxiii. p. 215 (May 1914).

The general covariancy of the equations is the great achievement of Einstein and Grossmann's theory.

Leeds, July 1914.

XI. *On the Form of a Suspended Wire or Tape including the Effect of Stiffness.* By ALFRED ERNEST YOUNG, *Assoc. Mem. Inst. C.E., Fellow of City Guilds Institute, late Deputy Surveyor-General in the Federated Malay States* [*].

IN the Philosophical Magazine for July 1903 there appeared a paper by Professor Richard C. Maclaurin on " The Influence of Stiffness on the Form of a Suspended Wire or Tape," the opening paragraph of which states :—

" Some of the greatest improvements in modern surveying are due to the substitution of a steel tape or wire for the old surveyor's chain. The newer instrument can, with proper precautions, be made an exceedingly accurate measurer of distances. So minute have been the corrections applied in some recent surveys, that it it has been questioned whether we may, with propriety, any longer regard the form in which the ' chain ' hangs as a catenary. It is true that the surveyor's tape is so thin as to be very flexible, but for some purposes there are advantages in using a circular wire, which is, of course, more rigid than the tape for the same weight. It may be thought that, at any rate for the circular wire, the hypothesis of perfect flexibility (on which the investigation of the form of the catenary rests) may introduce an error comparable with those for which corrections are applied in the best modern surveys. The object of this paper is to settle the matter by investigating the correction that must be applied when the rigidity of the tape or wire is taken into account."

* Communicated by the Author.

Professor Maclaurin then proceeds to form from first principles the differential equation for the curve in which a flexible wire hangs under its own weight and an applied tension. This equation, which is of the fourth order, he proceeds to solve by approximation, and eventually arrives at a formula for the effect of stiffness on the ' Sag Correction ' as deduced from the ordinary catenary formula. In an example which would be considered extreme in survey practice, *i. e.* a steel tape 10 chains long, $\frac{1}{8}$ inch wide, $\frac{1}{50}$ inch thick, wholly suspended under an end tension of 14 lb., this formula gives a stiffness correction of only 0·000000023 inch —equivalent to 0·184 inch in a million miles—from which Professor Maclaurin concludes that the neglect of the stiffness of the chain need cause little anxiety to the surveyor.

Before the writer had seen Professor Maclaurin's paper, his attention had been drawn to the effect of stiffness while he was engaged in measuring with a steel tape a base line in connexion with the Trigonometrical Survey of the Federated Malay States, and he had worked out a formula for this correction on the assumption that the sag was small, as it generally is in practice. The tape was in fact regarded as an elastic beam subjected to an end tension in addition to its own weight, and supported "clamped" or "free" at the ends. On comparing his results with Professor Maclaurin's, they were found not to agree, and for many years the writer was unable to account for the discrepancy, failing to discover any flaw in Professor Maclaurin's investigation or his own. He at length handed over the question to an assistant, Mr. D. T. Sawkins, B.A. (Cantab.), who was employed for some time in the Malay States Survey Department as a surveyor, and who succeeded in discovering the cause of the discrepancy, which appears to be due to Professor Maclaurin having neglected to use the complementary function in the approximate solution of his differential equation. This complementary function comprises the larger part of the correction, and though the whole correction is so small as to be seldom or never appreciable in practice, it is much larger than would appear from Professor Maclaurin's paper. The object of the present paper is to investigate the correct formula for the stiffness correction, to show where the error occurred in Professor Maclaurin's solution ; afterwards to give some results in the general catenary formula and its variation when the elastic *extension* of the tape is taken into account ; and, finally, to give the sag correction when a heavier tape is included in the series

in sag, which results the writer thinks may be of interest and perhaps of utility to those engaged in making surveys with the long steel tape.

That a steel tape is not perfectly flexible is easily seen by the surveyor. If it were, a small piece held out in the fingers would at once droop like a piece of thread, and if a long tape were suspended in several sags or bays over supports, it would drop away from the supports leaving a sharp point or cusp thereat, but on the contrary, even with the thinnest tape there is a distinct crest of curvature concave downwards at each support, with points of contrary flexure at some little distance on each side. The influence of the rigidity is to decrease the sag in either case, but it will easily be seen that the effect must be greater when the ends are bent over supports than it is when the tape is simply suspended at the ends with no bending moments at or points of contrary flexure near them.

We will first take the case originally solved by the writer of a long thin tape stretched by a large tension so that the sag is quite small, and with its ends supported at the same level so that the chord is horizontal. The tape is then symmetrical about its centre, and it will be convenient to use Cartesian coordinates, the axis of x being horizontal and tangent to the tape at its lowest point and the axis of y vertical through the same point.

(Fig. 1.) Let l be the length of the whole tape, w its
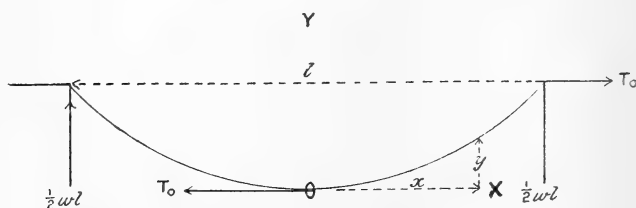
FIG. 1.

weight per unit of length, T_0 the horizontal component of the applied tension or, which is the same thing, the actual tension at the lowest point, and M_0 the unknown bending moment at the lowest point. Taking M_0 as positive when it tends to produce curvature convex to the axis of x, the bending moment at any point distant x from the origin is

$$M = M_0 + T_0 y - \frac{wx^2}{2}.$$

Since the curvature is supposed to be small, we may put $\dfrac{d^2y}{dx^2} = \dfrac{M}{EI}$, where E is Young's Modulus and I is the moment of inertia of the cross section, which gives

$$\frac{d^2y}{dx^2} - \frac{T_0 y}{EI} = \frac{M_0}{EI} - \frac{wx^2}{2EI}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

The well-known solution of this differential equation is

$$y = A \sinh\sqrt{\frac{T_0}{EI}}\,x + B \cosh\sqrt{\frac{T_0}{EI}}\,x - \frac{M_0}{T_0} + \frac{wx^2}{2T_0} + \frac{wEI}{T_0^2}, \quad (2)$$

where A and B are constants to be determined by the end conditions. Since $y = 0$ and $\dfrac{dy}{dx} = 0$ when $x = 0$, we have $B = \dfrac{M_0}{T_0} - \dfrac{wEI}{T_0^2}$ and $A = 0$, so that

$$y = \left(\frac{M_0}{T_0} - \frac{wEI}{T_0^2}\right)\left(\cosh\sqrt{\frac{T_0}{EI}}\,x - 1\right) + \frac{wx^2}{2T_0}. \quad \cdot \quad (3)$$

The value of M_0 will differ according as the ends are "free" or constrained so that the tangent to the tape is horizontal thereat. In the former case there will be no bending moment at the ends or $\dfrac{d^2y}{dx^2} = 0$ when $x = \dfrac{l}{2}$; and in the latter the slope will be zero at the ends or $\dfrac{dy}{dx} = 0$ when $x = \dfrac{l}{2}$.

Taking first the case of free ends, we have

$$\frac{d^2y}{dx^2} = \frac{T_0}{EI}\left(\frac{M_0}{T_0} - \frac{wEI}{T_0^2}\right)\cosh\sqrt{\frac{T_0}{EI}}\,\frac{l}{2} + \frac{w}{T_0} = 0$$

and

$$M_0 = \frac{wEI}{T_0}\left[1 - \frac{1}{\cosh\sqrt{\dfrac{T_0}{EI}}\cdot\dfrac{l}{2}}\right].$$

Inserting this value in equation (3) we have

$$y = -\frac{wEI}{T_0^2}\frac{\left(\cosh\sqrt{\dfrac{T_0}{EI}}\,x - 1\right)}{\cosh\sqrt{\dfrac{T_0}{EI}}\,\dfrac{l}{2}} + \frac{wx^2}{2T_0}. \quad \cdot \quad \cdot \quad (4)$$

H 2

To find the sag correction we have with sufficient accuracy $s - x = \dfrac{1}{2} \displaystyle\int \left(\dfrac{dy}{dx} \right)^2 dx$, and in the present case for the sag correction over the whole span we have

$$2(s - x) = \int_0^{\frac{l}{2}} \left(\frac{dy}{dx} \right)^2 dx.$$

Putting for simplicity $\sqrt{\dfrac{T_0}{EI}} = a$, we have

$$\frac{dy}{dx} = -\frac{w \sinh ax}{a T_0 \cosh \dfrac{al}{2}} + \frac{wx}{T_0},$$

and $\displaystyle\int_0^{\frac{l}{2}} \left(\frac{dy}{dx} \right)^2 dx$

$$= \frac{w^2}{T_0^2} \int_0^{\frac{l}{2}} \left(x^2 - \frac{2x \sinh ax}{a \cosh \dfrac{al}{2}} + \frac{\sinh^2 ax}{a^2 \cosh^2 \dfrac{al}{2}} \right) dx$$

$$= \frac{w^2}{T_0^2} \left[\frac{x^3}{3} - \frac{2x \cosh ax}{a^2 \cosh \dfrac{al}{2}} + \frac{2 \sinh ax}{a^3 \cosh \dfrac{al}{2}} + \frac{\sinh 2ax}{4a^3 \cosh^2 \dfrac{al}{2}} - \frac{x}{2a^2 \cosh^2 \dfrac{al}{2}} \right]_0^{\frac{l}{2}}$$

$$= \frac{w^2}{T_0^2} \left[\frac{l^3}{24} - \frac{l}{a^2} + \frac{5 \tanh \dfrac{al}{2}}{2a^3} - \frac{l}{4a^2 \cosh^2 \dfrac{al}{2}} \right]. \quad \cdots \cdots \quad (5)$$

The first term of this expression $\dfrac{w^2 l^3}{24 T_0^2}$ is independent of the stiffness, and is the ordinary sag correction on the supposition that the curve in which the tape hangs is the catenary or, which is the same thing to the order given, the parabola or circle. The remaining terms give the correction to this due to the stiffness. When dimensions are given in inches the quantity a is of the order 5 in ordinary surveyors' tapes ; in the example taken by Professor Maclaurin, a $\frac{1}{8}$ in. tape under 14 lb. tension, $a = 3 \cdot 1$. Taking l in the same unit, it will be seen that both $\sinh \dfrac{al}{2}$ and $\cosh \dfrac{al}{2}$ are sensibly equal to $\frac{1}{2} e^{\frac{al}{2}}$ and enormously large, so that $\tanh \dfrac{al}{2} = 1$. The third term can therefore be neglected in comparison

with the second, since the latter is at least l times (in inches) larger, and the fourth term is quite inappreciable. The correction for stiffness is in this case, therefore, given by

$$\frac{w^2 l}{a^2 T_0{}^2} = \frac{w^2 l \mathrm{EI}}{T_0{}^3}, \quad \cdots \cdots \quad (6)$$

which is to be subtracted from the catenary sag correction. Professor Maclaurin's expression for the correction is

$$\frac{w\mathrm{EI}}{2T_0{}^2}\left[\phi - \frac{\tan\phi(2 - \sec^2\phi)}{\sec^4\phi}\right] \text{ where } \phi = \sin^{-1}\frac{wl}{2T_0}.$$

Expanding this expression in terms of ϕ, which we may put equal to $\frac{wl}{2T_0}$, we get for the correction $\frac{w^4 l^3 \mathrm{EI}}{6T_0{}^5}$, which is equal to the writer's expression multiplied by $\frac{1}{6}\left(\frac{wl}{T_0}\right)^2$. In the example taken by Professor Maclaurin, $l = 10$ chains $= 7920$ inches, width $= \frac{1}{3}$ in., thickness $= \frac{1}{60}$ in., $w = 0\cdot000564$ lb. per inch, $\mathrm{E} = 3 \times 10^7$ lb. per square inch, $\mathrm{T} = 14$ lb. From which, since $\mathrm{I} = \frac{1}{12}bt^3$ we deduce

$$a = \sqrt{\frac{T_0}{\mathrm{EI}}} = 3\cdot110, \ a^2 = 9\cdot67, \ \frac{wl}{T} = 0\cdot3192,$$

so that

$$\frac{w^2 l \mathrm{EI}}{T_0{}^3} = \frac{0\cdot3192^2}{7920 \times 9\cdot67} = 0\cdot00000131 \text{ inch,}$$

which though quite inappreciable is about 60 times as great as Professor Maclaurin's value. In working this example T_0 has been taken $= T = 14$ lb., though, strictly speaking,

$$T_0{}^2 = T^2 - \frac{w^2 l^2}{4},$$

or

$$T_0 = T\left(1 - \frac{1}{8}\left(\frac{wl}{T}\right)^2\right) \text{ nearly} = 13\cdot84 \text{ lb.}$$

The effect of the stiffness on the form of the tape is best seen perhaps from the expression for the tangent of the slope,

$$\frac{dy}{dx} = \frac{w}{T_0}\left(x - \frac{\sinh ax}{a\cosh\frac{al}{2}}\right).$$

The first part shows that the curve is a parabola with vertex downwards, the second is the alteration to this caused by the stiffness which tends to make the slope less, the effect

increasing as we approach the ends, where it attains a maximum value of

$$\frac{w \tanh \dfrac{al}{2}}{a\mathrm{T}_0} = \frac{w}{a\mathrm{T}_0}, \text{ practically.}$$

Since in the example taken $a = 3\cdot11$ the maximum effect in this case is only $2''\cdot7$ in a slope of about $9° 9'$. The effect can be also seen by reckoning x from the end instead of the middle of the tape and writing $x' = \dfrac{l}{2} - x$, so that

$$\frac{dy}{dx} = \frac{w}{\mathrm{T}_0}\left[\frac{l}{2} - x' - \frac{\sinh a\left(\dfrac{l}{2} - x'\right)}{a \cosh \dfrac{al}{2}} \right] = \frac{w}{\mathrm{T}_0}\left[\frac{l}{2} - x' - \frac{1}{ae^{ax'}} \right], \text{ very nearly,}$$

putting $\tanh \dfrac{al}{2} = 1$. Since $e^{3\cdot11} = 22$ nearly this shows that at only 1 inch from the end the effect of stiffness on the slope is reduced to $\frac{1}{22}$ of its maximum value, *i.e.*, to about $\frac{1}{10}$ of a second of arc.

We will now consider the case of ends clamped or constrained so that the tangent to the tape is horizontal thereat, in which not only is the effect of stiffness greater but the conditions approach more nearly those found in practice, because, in using the long steel tape, the surveyor generally supports it at several points forming several bays in sag, the tangent to the tops at each point of support being horizontal, and a bending moment with curvature concave to the axis of x occurring thereat. Putting then $\dfrac{dy}{dy} = 0$ where $x = \dfrac{l}{2}$ in equation (3), we get

$$0 = \left(\frac{a\mathrm{M}_0}{\mathrm{T}_0} - \frac{w}{a\mathrm{T}_0} \right) \sinh \frac{al}{2} + \frac{wl}{2\mathrm{T}_0},$$

or

$$\mathrm{M}_0 = \frac{w}{a^2}\left(1 - \frac{al}{2\sinh \dfrac{al}{2}} \right).$$

Substituting this in (3) we get

$$y = \frac{w}{\mathrm{T}_0}\left[\frac{x^2}{2} - \frac{l(\cosh ax - 1)}{2a \sinh \dfrac{al}{2}} \right] \quad . \quad . \quad . \quad . \quad (7)$$

$$\frac{dy}{dx} = \frac{w}{\mathrm{T}_0}\left[x - \frac{l \sinh ax}{2\sinh \dfrac{al}{2}} \right],$$

and $\displaystyle\int_0^{\frac{l}{2}} \left(\frac{dy}{dx}\right)^2 dx$

$$= \frac{w^2}{T_0^2} \int_0^{\frac{l}{2}} \left[x^2 - \frac{lx \sinn ax}{\sinh \dfrac{al}{2}} + \frac{l^2 \sinh^2 ax}{4 \sinh^2 \dfrac{al}{2}} \right] dx$$

$$= \frac{w^2}{T_0^2} \left[\frac{x^3}{3} - \frac{lx \cosh ax}{a \sinh \dfrac{al}{2}} + \frac{l \sinh ax}{a^2 \sinh \dfrac{al}{2}} + \frac{l^2 \sinh 2ax}{16a \sinh^2 \dfrac{al}{2}} - \frac{l^2 x}{8 \sinh^2 \dfrac{al}{2}} \right]_{}^{\frac{l}{2}}.$$

$$= \frac{w^2}{T_0^2} \left[\frac{l^3}{24} - \frac{3l^2}{8a \tanh \dfrac{al}{2}} + \frac{l}{a^2} - \frac{l^3}{16 \sinh^2 \dfrac{al}{2}} \right] \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (8)$$

The third term can be neglected in comparison with the second and the fourth is quite inappreciable, so that in this case the correction for stiffness is

$$- \frac{3w^2 l^2}{8T_0^2 a} = - \frac{3}{8} \left(\frac{wl}{T_0}\right)^2 \sqrt{\frac{EI}{T_0}}.$$

This is $\dfrac{3}{8} l \sqrt{\dfrac{T_0}{EI}}$ times the correction for free ends, and in the example considered is $\dfrac{3 \times 7920 \times 3\cdot11}{8} = 9237$ times as great $= 0\cdot012$ inch in the 10 chains, a quantity which would be worth considering in base-line measurement, though it would not be likely of course that such a large bay as 10 chains in sag would occur in such an operation.

Writing $x = \dfrac{l}{2} - x'$ in the expression for $\dfrac{dy}{dx}$, it reduces to

$$\frac{dy}{dx} = \frac{w}{T_0} \left[\frac{l}{2} - x' - \frac{l}{2e^{ax'}} \right],$$

so that when $x' = 0$ at the support, the effect of the stiffness is equal to $\dfrac{wl}{2T_0} = 9° \, 9'$ in the example. To find the bending-moment at the support we have

$$M = EI \frac{d^2 y}{dx^2}$$

$$= \frac{w}{a^2} \left[1 - \frac{al}{2 \tanh \dfrac{al}{2}} \right] = \frac{w}{a^2} \left(1 - \frac{al}{2}\right) \text{ nearly, } = - \frac{wl}{2a} \text{ practically.}$$

The point of contrary flexure can be found by solving for x or x' from the equation

$$\frac{d^2y}{dx^2} = 0 \quad \text{or} \quad \frac{al \cosh a\left(\frac{l}{2} - x'\right)}{2 \sinh \dfrac{al}{2}} = 1,$$

whence

$$x' = \frac{\log_e \dfrac{al}{2}}{a} = \frac{2\cdot 30 \log_{10} \dfrac{al}{2}}{a} = 3\cdot 6 \text{ inches in the example.}$$

In this short distance the effect of the stiffness on the slope has decreased from $9° 9'$ to about $0''\cdot 5$, which shows how rapidly this effect dies away.

If we make $x = \dfrac{l}{2}$ in the expressions for y we obtain the deflexion of the middle point of the tape below the ends, and if we make $T_0 = 0$ in these resulting expressions we should obtain the deflexion of the middle point of a beam loaded uniformly and supported at the ends either free or clamped. In the first case we have

$$y = \frac{wx^2}{2T_0} - \frac{w}{a^2}\frac{\cosh ax - 1}{\cosh \dfrac{al}{2}} = \frac{wl^2}{8T_0} - \frac{w}{a^2}\left(1 - \operatorname{sech}\frac{al}{2}\right)$$

$$= \frac{wl^2}{8T_0} - \frac{w}{a^2}\left(1 - 1 + \frac{a^2l^2}{8} - \frac{5a^4l^4}{384} + \text{ terms involving } T_0^3\right)$$

$$= \frac{5}{384}\frac{wl^4}{EI} \quad \text{when} \quad T_0 = 0.$$

In the second case, we have

$$y = \frac{w}{T_0}\left[\frac{l^2}{8} - \frac{l\left(\cosh\dfrac{al}{2} - 1\right)}{2a \sinh\dfrac{al}{2}}\right] = \frac{w}{T_0}\left[\frac{l^2}{8} - \frac{l \tanh\dfrac{al}{4}}{2a}\right]$$

$$= \frac{w}{T_0}\left[\frac{l^2}{8} - \frac{l}{2a}\left(\frac{al}{4} - \frac{a^3l^3}{192} + \text{ terms involving } a^5 \text{ and higher powers}\right)\right]$$

$$= \frac{wl^4}{384EI}, \quad \text{when} \quad T_0 = 0.$$

These results agree with those given in books on Applied Mechanics.

In the preceding investigation we have assumed that the tape is used on level ground, and also that the tension used is so great that the curve in which the tape hangs is so flat that even at the ends we may consider $\sin \psi$ and $\tan \psi = \psi$ where ψ is the angle of slope. The greatest value of this angle is $\frac{1}{2} \frac{wl}{T}$ where l is the whole length of the tape, and we have seen that with a $\frac{1}{5}$ in. tape 10 chains long under the rather low tension of 14 lb. this angle is only about 9° when the whole 10 chains is in sag. In actual practice, however, tapes are used on considerable slopes up to 45°, or even 60°, with the horizontal. It might be assumed, and it will be proved later, that the ordinary sag-correction—defined as the difference between the curve and its chord—can be obtained in these cases by writing $w \cos \psi$ for w in the formula $\frac{w^2 l^3}{24 T^2}$, and the same remark applies to the correction for stiffness because, even in the extreme case of constrained ends, the angle through which the tape is bent is not the whole angle ψ but the difference between the slope of the chord and ψ, and this angle is less the steeper the slope, being given sufficiently closely by $\frac{1}{2} \frac{wl \cos \psi}{T}$. So far as the correction for stiffness is concerned, therefore, the case of chord horizontal is the most unfavourable that occurs in survey practice, and the solution found can be used for slopes even steeper than that in Professor Maclaurin's example. But we will now proceed to consider the general case dealt with by Professor Maclaurin.

(Fig. 2.) Professor Maclaurin starts with the following
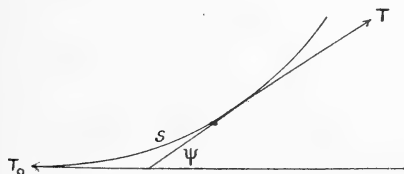
FIG. 2.

fundamental equations of equilibrium of a small element of the tape :

$$\frac{dT}{ds} - U \frac{d\psi}{ds} - w \sin \psi = 0 \quad . \quad . \quad . \quad . \quad (11)$$

$$T \frac{d\psi}{ds} + \frac{dU}{ds} - w \cos \psi = 0 \quad . \quad . \quad . \quad . \quad (12)$$

$$\frac{dL}{ds} + U = 0 . \quad . \quad . \quad . \quad (13)$$

Moreover, $L = EI/\rho = EI \dfrac{d\psi}{ds}$, which with (13) gives

$$EI \frac{d^2\psi}{ds^2} + U = 0. \quad \ldots \ldots \quad (14)$$

In these equations T is the tension, U the shear, L the bending-moment, s the length of the curve measured along the arc from some fixed point, ψ the angle the tangent makes with the horizontal, $1/\rho$ the curvature, w the weight of the tape per unit length, E Young's Modulus, and I the moment of inertia of a cross-section of the tape about a line through its centre of gravity perpendicular to the plane in which the tape hangs.

Eliminating L, U, and T, the following is the differential equation arrived at for the curve in which the tape hangs:

$$\cos\psi \frac{\ddot{\psi}}{\dot{\psi}^2} + 2\sin\psi = \frac{EI}{w}\left[\dot{\psi}\dddot{\psi} + \frac{\ddddot{\psi}\dot{\psi} - \dddot{\psi}\ddot{\psi}}{\dot{\psi}^2}\right] \quad . \quad (15)$$

where the dot $\cdot$ denotes differentiations with respect to s.

When the tape is perfectly flexible the right-hand side of (15) is zero, and we get

$$\cos\psi \frac{\ddot{\psi}}{\dot{\psi}^2} + 2\sin\psi = 0,$$

whence $\dfrac{\ddot{\psi}}{\dot{\psi}^2} = -2\tan\psi$; $1/\rho = \dot{\psi} = \dfrac{\cos^2\psi}{c}$,

which of course represents the common catenary.

The flexibility of the surveyor's tape being so nearly perfect, Professor Maclaurin proceeds to solve (15) by approximation, substituting $\dot{\psi} = \dfrac{\cos^2\psi}{c}$ in the right-hand side of (15), and finally arrives at the following for the intrinsic equation of the curve :

$$s = c\tan\psi + \frac{2EI}{wc^2}\sin\psi\cos^2\psi. \quad \ldots \quad (16)$$

From this, after further transformations, he finally derives the formula for the stiffness correction previously quoted, viz.,

$$\frac{EI}{4wc^2}\left[\phi - \tan\phi\frac{(2-\sec^2\phi)}{\sec^4\phi}\right],$$

where $\phi = \sin^{-1}\dfrac{wl}{2T_0}$ and $c^2 = \dfrac{T_0^2}{w^2}$.

The investigation and formulæ contain no stipulation as to the end conditions.

Mr. Sawkins pointed out that multiplying each member of equation (15) by cos ψ, each is a perfect differential, which Professor Maclaurin does not seem to have noticed.

Integrating them we have

$$\frac{w\cos^2\dot{\psi}}{\dot{\psi}} = -\mathrm{EI}\left(\frac{\dddot{\psi}}{\dot{\psi}}\cos\psi + \ddot{\psi}\sin\psi\right) + \mathrm{A}, \quad . \quad (17)$$

where A is a constant of integration. Putting $\psi=0$ in this and equation (12), we see that A is the tension at the point $\psi=0$ if there is such a point, *i. e.*, the horizontal component of the tension $=\mathrm{T}_0$.

Integrating again, we find

$$ws = -\mathrm{EI}\frac{\ddot{\psi}}{\cos\psi} + \mathrm{T}_0\tan\psi + \mathrm{B}. \quad . \quad . \quad (18)$$

If we take the origin so that $s=0$ when $\psi=0$, then $\mathrm{B}=0$; so finally

$$\mathrm{EI}\frac{d^2\psi}{ds^2} = -ws\cos\psi + \mathrm{T}_0\sin\psi, \quad . \quad . \quad (19)$$

which is the equation to be solved in the general case.

This equation might have been derived straight away from statical considerations. It is simply the statement of Professor Maclaurin's (14) that the differential coefficient of the bending-moment is equal to the shearing force which is evidently equal to $\mathrm{T}_0\sin\psi - ws\cos\psi$, where T_0 is the horizontal component of the tension or the tension at the point $\psi=0$ and s is measured from the same point. In actual practice, when the tape is used on a slope there may not actually be such a point, but in applying the formulæ which follow, the tape is supposed to be continued to such an imaginary point from which the distances s are supposed to be measured. The actual length l of the tape is in such cases either s_2+s_1 or s_2-s_1 according as the vertex of the curve occurs in the tape or not. When s_1 is equal and opposite to s_2, we have the symmetrical case or case with chord horizontal.

If in equation (19) we put $\cos\psi=1$ and $\sin\psi=\psi$, we have

$$\mathrm{EI}\frac{d^2\psi}{ds^2} - \mathrm{T}_0\psi = ws,$$

or

$$\frac{d^2\psi}{ds^2} - \frac{\mathrm{T}_0}{\mathrm{EI}}\psi = -\frac{ws}{\mathrm{EI}},$$

whence

$$\psi = \text{A} \sinh as + \text{B} \cosh as + \frac{ws}{\text{T}_0}, \quad \text{where } a^2 = \frac{\text{T}_0}{\text{EI}},$$

$$= \text{A} \sinh as + \frac{ws}{\text{T}_0}, \quad \text{since B}=0 \text{ with } s=0 \text{ for } \psi=0.$$

And since

$$x = \int \cos \psi \, ds = \int \left(1 - \frac{\psi^2}{2} + \ldots \right) ds,$$

we have the sag correction

$$= 2(s-x) = \int_0^{\frac{l}{2}} \psi^2 ds,$$

$$= \int_0^{\frac{l}{2}} \left[\frac{w^2 s^2}{\text{T}_0{}^2} + \frac{2\text{A}ws}{\text{T}_0} \sinh as + \text{A}^2 \sinh^2 as \right] ds,$$

$$= \frac{w^2 l^3}{24\text{T}_0{}^2} + \frac{2\text{A}w}{\text{T}_0} \left(\frac{l \cosh \dfrac{al}{2}}{2a} - \frac{\sinh \dfrac{al}{2}}{a^2} \right) + \text{A}^2 \left(\frac{\sinh al}{4a} - \frac{l}{4} \right).$$

In the case of constrained ends we have $\psi=0$ when $s = \frac{l}{2}$; hence

$$\text{A} = - \frac{wl}{2\text{T}_0 \sinh \dfrac{al}{2}},$$

and sag correction

$$= \frac{w^2}{\text{T}_0{}^2} \left[\frac{l^3}{24} - \frac{3l^2}{8a \tanh \dfrac{al}{2}} + \frac{l}{a^2} - \frac{l^3}{16 \sinh^2 \dfrac{al}{2}} \right],$$

the same as already found by the Cartesian method.

If in equation (19) we put as a first approximation

$$\text{EI} \frac{d^2 \psi}{ds^2} = 0,$$

we find

$$\tan \psi = \frac{ws}{\text{T}_0},$$

or

$$\psi = \tan^{-1} \frac{ws}{\text{T}_0} = \tan^{-1} \frac{s}{c};$$

hence

$$\frac{d\psi}{ds} = \frac{\cos^2 \psi}{c}, \quad \text{and} \quad \frac{d^2\psi}{ds^2} = - \frac{2 \sin \psi \cos^3 \psi}{c^2}.$$

$$\therefore \quad -2\text{EI} \frac{\sin \psi \cos^3 \psi}{c^2} = -ws \cos \psi + \text{T}_0 \sin \psi.$$

Hence $$s = c \tan \psi + \frac{2EI}{wc^2} \sin \psi \cos^3 \psi,$$

which is precisely the value arrived at by Professor Maclaurin, but in deriving this we have neglected altogether the complementary function of our differential equation. The fallacy here involved is so subtle that the writer wonders if a parallel case has occurred in any other physical investigation. The only somewhat similar case he has come across is in the investigation of the Earth's Precession (see Routh's 'Rigid Dynamics,' vol. ii. p. 325, Ed. 1892), but there it is shown that the original neglect of the complementary function has not vitiated the result. He will think himself fortunate if this paper should induce investigators to give more careful attention to the question.

The effect of the stiffness can be seen more clearly by dividing the angle ψ into two parts, one of which ϕ is the angle due to the ordinary catenary action, and the other θ the correction to this due to the stiffness. We have, then, $\psi = \phi + \theta$,

where $$\phi = \tan^{-1} \frac{ws}{T_0} = \tan^{-1} bs,$$

putting $b = \dfrac{w}{T_0}$.

Equation (19) becomes

$$\frac{EI}{T_0} \frac{d^2(\phi + \theta)}{ds^2} = -bs \cos \psi + \sin \psi = \sec \phi \sin \theta,$$

or $$\frac{d^2(\phi + \theta)}{ds^2} = a^2 \sec \phi \sin \theta \; ;$$

but

$$\frac{d^2\phi}{ds^2} = -\frac{2b^3 s}{(1 + b^2 s^2)^2}, \quad \text{and} \quad \sec \phi = (1 + b^2 s^2)^{\frac{1}{2}}.$$

$$\therefore \quad \frac{d^2\theta}{ds^2} = a^2 (1 + b^2 s^2)^{\frac{1}{2}} \sin \theta + \frac{2b^3 s}{(1 + b^2 s^2)^2} . \quad \cdot \quad \cdot \quad (20)$$

This or equation (19) must be solved for the complete general case, but the writer has not been able to find the general solution of either. In the surveyor's tape θ will always be a very small angle, even with steep slopes and a low tension, so that we may put θ for $\sin \theta$ and solve (20) by approximation. Neglecting $b^2 s^2$ in comparison with unity we have

$$\frac{d^2\theta}{ds^2} - a^2\theta = 2b^3 s,$$

whence $\qquad \theta = A \sinh as + B \cosh as - \dfrac{2b^3 s}{a^2}$;

and since $\theta = 0$ when $\psi = 0$ and $s = 0$, we have $B = 0$.

Thus $\qquad \theta = A \sinh as - \dfrac{2b^3 s}{a^2}$,

and $\qquad \psi = \phi + \theta = \tan^{-1} bs + A \sinh as - \dfrac{2b^3 s}{a^2}$.

Also

$$x = \int \cos \psi \, ds = \int (\cos \phi \cos \theta - \sin \phi \sin \theta) \, ds$$
$$= \int \cos \phi \, ds - \int \left(\frac{\theta^2}{2} + \theta \sin \phi \right) ds \ \text{ nearly.}$$

The first integral is the ordinary catenary formula, and the second is the correction to this due to the rigidity. If we put $\tan^{-1} bs$ and $\sin \phi = bs$ as a first approximation and neglect $\dfrac{2b^3 s}{a^2}$ in comparison with bs, we find A from the equation $\psi = bs + A \sinh as$, and then the sag correction due to the rigidity is given by

$$2 \int_0^{\frac{l}{2}} \left(Abs \sinh as + \tfrac{1}{2} A^2 \sinh^2 as - \frac{2b^4 s^2}{a^2} \right) ds.$$

The first two terms will be found to give the expressions already quoted, and the last gives

$$- \frac{b^4 l^3}{6a^2} = - \frac{w^4 l^3 EI}{6 T_0{}^5} ,$$

which is the value found by Professor Maclaurin.

Through the kindness of Professor H. H. Turner, F.R.S., the writer is indebted to Professor A. R. Forsyth, F.R.S., for suggesting the following method of carrying the approximation further.

Write $\qquad \theta = A \sinh as - \dfrac{2b^3 s}{a^2} + v$

and substitute this in equation (20) expanded to the first term in $b^2 s^2$, or

$$\frac{d^2 \theta}{ds^2} = a^2 (1 + \tfrac{1}{2} b^2 s^2) \left(\theta - \frac{\theta^3}{6} \right) + 2b^3 s (1 - 2b^2 s^2) \ ;$$

we have

$$\frac{d^2 v}{ds^2} - a^2 v = \frac{1}{2} a^2 b^2 A s^2 \sinh as - \frac{a^2}{6} A^3 \sinh^3 as - 5b^5 s^3,$$

of which the particular integral only is required, as the complementary function has already occurred in the approximate solution. The particular integral of the first term is found to be

$$\frac{Ab^2}{6a^2}\left\{ \left(\tfrac{1}{2}a^3s^3 + \tfrac{3}{4}as\right)\cosh as - \left(\tfrac{3}{4}a^2s^2 + \tfrac{3}{8}\right)\sinh as \right\} *,$$

of the second

$$-\frac{A^3}{96}\left(\frac{\sinh 3as}{2} + 3\sinh as - 6as\cosh as\right),$$

and of the third

$$+\frac{5b^5s^3}{a^2} + \frac{30b^5s}{a^4}.$$

The full expression for ψ as far as terms in s^3 is thus

$$\psi = bs - \frac{b^3s^3}{3} + \ldots + A\left[\sinh as + \frac{b^2}{12a^2}\left\{\left(a^3s^3 + \frac{3as}{2}\right)\cosh as\right.\right.$$
$$\left.\left. - \left(\frac{3a^2s^2}{2} + \frac{3}{4}\right)\sinh as\right\}\right]$$

$$-\frac{A^3}{96}\left(\tfrac{1}{2}\sinh 3as + 3\sinh as - 6as\cosh as\right)$$

$$-\frac{2b^3s}{a^2} + \frac{5b^5s^3}{a^2} + \frac{30b^5s}{a^4} - \ldots \quad . \quad (21)$$

It is remarkable that the coefficient of $\cosh as$ in the expression by A, viz., $\dfrac{b^2as^3}{12} = \dfrac{b^2s^2as}{12}$ is in ordinary cases greater than unity and so greater than the coefficient of $\sinh as$ in the first term. For instance, in the example already quoted the greatest value of the coefficient for $s = 5$ chains $= 3960$ inches, $bs = 0\cdot1596$, $a = 3\cdot11$ is

$$\frac{b^2s^2as}{12} = \frac{0\cdot1596^2 \times 3\cdot11 \times 3960}{12} = 26\cdot2.$$

This will give a smaller value for A when the end conditions are put in, but the value of the term by A is again increased by this factor, so that the expression for the alteration in the sag correction due to the stiffness is not altered in the most important term. This has been tested by forming $\displaystyle\int_0^{\frac{l}{2}} \psi^2 ds$ from the expression

$$\psi = bs + A\left(\sinh as + \frac{ab^2s^3\cosh as}{12}\right)$$

---

* This particular integral was also found by Mr. Sawkins, to whom the device of dividing ψ into ϕ and θ is due, by another method.

for both free and constrained ends. By continuing the expansion of $(1 + b^2 s^2)^{\frac{1}{2}}$ it appears that the integral by A can be written

$$A\left[\sinh as + \frac{as \cosh as}{4}\left(\frac{b^2 s^2}{3} - \frac{b^4 s^4}{4\cdot5} + \frac{b^6 s^6}{8\cdot7} - \cdots\right)\right],$$

which shows that further terms rapidly decrease. The rest of the factors in (21) appear to be all of a smaller order than those of the first approximation.

This is as far as the writer has been able to carry the investigation, and though it has not been found possible to obtain a general solution of either equation (19) or (20) he ventures to think that, so far as the surveyor's tape is concerned, he has shown that the approximate solution first derived is sufficient, and proves that if only an adequate tension is used and the lengths of the bays in sag are not extreme, the effect of stiffness on the sag correction is quite negligible.

The General Catenary Formula.

The ordinary catenary formula as applied to surveyors' tapes has been worked out fairly completely both when the tape is considered inextensible and when the elastic extension due to the tension is taken into account. An able and useful paper on " A System of Accurate Measurement by means of long Steel Ribands " was read before the Royal Society of New South Wales in 1885 by Mr. G. H. Knibbs, C.M.G., formerly Professor of Surveying at Sydney University, and now Commonwealth Statistician, in which formulæ are given for the cases of chord both horizontal and inclined, but applying more particularly to the method by which the sag correction is eliminated by altering the tension, a method of chaining which has, however, not been found very convenient in practice, the more usual process being to preserve a constant end tension and calculate corrections. Another paper, on " The Measurement of Distances with Long Steel Tapes," was read by Mr. C. W. Adams, Chief Surveyor, Blenheim, New Zealand, before the Victorian Institute of Surveyors in 1888. In this the series for the sag correction in terms of the end tension is rigorously developed for a number of terms, and tables are supplied for use with various ratios of $\frac{wl}{T}$ and for various slopes. These papers contain practically all that is required by the surveyor engaged on all except the most refined traverse work. The theory as applied to Base-Line measurement and the effect of the elastic extension are dealt with in more detail in Appendix

No. 8 of the Report for 1892 of the United States Coast and Geodetic Survey. And lastly, in 1912 in No. 1, New Series, of the Professional Papers of the Ordnance Survey there appears a Discussion on the Theory of Measurement by Metal Tapes and Wires in Catenary, by Professor O. Henrici, F.R.S., and Captain E. O. Henrici, R.E. The last mentioned paper investigates thoroughly the effect of the elastic extension when the tape has been standardized in catenary under tension, and shows that there will then only be a very small correction when the tape is used on a slope. The sag formulæ in this paper apply also more particularly to the case where the tape is standardized in catenary and used in base-line measurement under the same conditions, the slopes being obtained by measuring the difference of level of the supports. It is desirable, however, to have formulæ which contain only quantities observed in the field, and in traverse work the surveyor generally uses a tape which has been standardized under a certain tension on the flat, and he usually applies the same tension in the field either at the upper or lower end when working on slopes. He observes on the vertical arc of his traversing theodolite the actual angle of slope or inclination of the chord of his tape, and the lengths of the bays in sag depend to a great extent on the ground he is working over.

The following investigation of the catenary at any angle is a development of that given in the above mentioned paper of Mr. Knibbs:

Let $s_1 s_2$, $x_1 x_2$, and $y_1 y_2$ refer to two points on the catenary, the subscript 2 referring to the higher, so that $s_2 - s_1 = l$ the whole length of the tape, and let k = the length of the chord of l and ζ the angle it makes with the vertical. We have then

$$y_2 = c \cosh \frac{x_2}{c}; \qquad y_1 = c \cosh \frac{x_1}{c};$$

$$s_2 = c \sinh \frac{x_2}{c}; \qquad s_1 = c \sinh \frac{x_1}{c};$$

$$s_2 - s_1 = l; \quad x_2 - x_1 = k \sin \zeta; \quad y_2 - y_1 = k \cos \zeta.$$

Therefore
$$k \cos \zeta = c \left(\cosh \frac{x_2}{c} - \cosh \frac{x_1}{c} \right),$$

$$l = c \left(\sinh \frac{x_2}{c} - \sinh \frac{x_1}{c} \right),$$

$$l^2 - k^2 \cos^2 \zeta = 2c^2 \left(\cosh \frac{x_2 - x_1}{c} - 1 \right) = 2c^2 \left(\cosh \frac{k \sin \zeta}{c} - 1 \right)$$

$$= k^2 \sin^2 \zeta + \frac{k^4 \sin^4 \zeta}{12 c^2} + \frac{k^6 \sin^6 \zeta}{360 c^4} + \cdots$$

Therefore

$$l^2 = k^2 + \frac{k^4 \sin^4 \zeta}{12c^2} + \frac{k^6 \sin^6 \zeta}{360c^4} + \frac{k^8 \sin^8 \zeta}{20160c^6} + \cdots \quad . \quad (22)$$

We have thus obtained a development for l the length of the tape in terms of k the chord, ζ the angle the chord makes with the vertical, and $c = \dfrac{T_0}{w}$ where T_0 is the unknown horizontal component of the tension.

By reversing the series we obtain the following development of k^2 in terms of l^2 :

$$k^2 = l^2 \left[1 - \frac{\sin^4 \zeta \, l^2}{12c^2} + \left(\frac{\sin^8 \zeta}{72} - \frac{\sin^6 \zeta}{360} \right) \frac{l^4}{c^4} \right.$$
$$\left. - \left(\frac{5 \sin^{12} \zeta}{1728} - \frac{\sin^{10} \zeta}{864} + \frac{\sin^8 \zeta}{20160} \right) \frac{l^6}{c^6} + \cdots \right] . \quad (23)$$

And by extracting the square root we obtain after reducing

$$k = l \left[1 - \frac{\sin^4 \zeta \, l^2}{24c^2} + \frac{\sin^6 \zeta \, l^4}{c^4} \left(\frac{3}{640} - \frac{7 \cos^2 \zeta}{1152} \right) \right.$$
$$\left. - \frac{\sin^8 \zeta \, l^6}{c^6} \left(\frac{5}{1728} - \frac{43 \cos^2 \zeta}{23040} + \frac{11 \cos^4 \zeta}{9216} \right) + \cdots \right] . \quad (24)$$

If we make $\zeta = 90°$ so that the chord is horizontal we have

$$k = l \left[1 - \frac{l^2}{24c^2} + \frac{3l^4}{640c^4} - \frac{5l^6}{7168c^6} + \cdots \right] = 2c \sinh^{-1} \frac{l}{2c} \quad . \quad (25)$$

as it ought to be ; and if we write for c^2 its value $\dfrac{T_0^2}{w^2} = \dfrac{T^2}{w^2} - \dfrac{l^2}{4}$ where T is the end tension, and then carry the correction due to $\dfrac{l^2}{4}$ to the next terms we find

$$k = l \left[1 - \frac{w^2 l^2}{24T^2} - \frac{11 w^4 l^4}{1920T^4} - \cdots \right] \quad . \quad . \quad (26)$$

which is the series given in Mr. Adams' paper quoted above and which can be written approximately

$$k = l \left[1 - \frac{w^2 l^2}{24T^2} - \frac{10}{3} \left(\frac{w^2 l^2}{24T^2} \right)^2 \right].$$

Returning to the general case we have to find an expression for c in terms of the end tension and the angle of slope. Considering the portion of tape let V_2 and V_1 be the vertical

components of the tension at the points 2 and 1, then we know that $V_2 - V_1 = wl$. If T_2 and T_1 are the full tensions

FIG. 3.

and $h = y_2 - y_1$ the difference in height between the points, we have

$$T_2{}^2 = w^2 c^2 + V_2{}^2 \; ; \quad T_1{}^2 = w^2 c^2 + V_1{}^2 \; ; \quad T_2 - T_1 = wh.$$

$$\therefore \quad T_2{}^2 - T_1{}^2 = V_2{}^2 - V_1{}^2 \; ;$$

$$\therefore \quad (T_2 + T_1) wh = (V_2 + V_1) wl \; ;$$

$$\therefore \quad (2T_2 - wh) h = (2V_2 - wl) l \; ;$$

$$\therefore \qquad V_2 = \frac{T_2 h}{l} + w\left(\frac{l^2 - h^2}{2l}\right); \quad . \quad . \quad (27)$$

and since $w^2 c^2 = T_2{}^2 - V_2{}^2$ we have

$$c^2 = \frac{T_2{}^2}{w^2}\left(1 - \frac{h^2}{l^2}\right)\left\{\left(1 - \frac{wh}{2T_2}\right)^2 - \frac{w^2 l^2}{4T_2{}^2}\right\} \quad . \quad . \quad (28)$$

as found by Professor and Captain Henrici.

Now we have to a first approximation $h = l \cos \zeta$, so we may write

$$c^2 = \frac{T_2{}^2}{w^2} \sin^2 \zeta \left\{\left(1 - \frac{wl \cos \zeta}{2T}\right)^2 - \frac{w^2 l^2}{4T^2}\right\}; \quad . \quad . \quad (29)$$

and if this be substituted in equation (24) we have

$$k = l\left[1 - \frac{w^2 l^2 \sin^2 \zeta}{24 T_2{}^2\left\{\left(1 - \frac{wl \cos \zeta}{2T}\right)^2 - \frac{w^2 l^2}{4T_2{}^2}\right\}}\right.$$

$$\left. + \frac{w^4 l^4 \sin^2 \zeta}{T_2{}^4\left\{\left(1 - \frac{wl \cos \zeta}{2T}\right)^2 - \frac{w^2 l^2}{4T_2{}^2}\right\}^2}\left(\frac{3}{640} - \frac{7 \cos^2 \zeta}{1152}\right) - \ldots\right]. \; (30)$$

I 2

We can now correct this expression for the assumption that $h = l \cos \zeta$ nearly, whereas $h = k \cos \zeta$ exactly.   Putting $\lambda = l - k$ we have strictly

$$c^2 = \frac{T_2^2}{w^2}\left(1 - \frac{(l-\lambda)^2 \cos^2 \zeta}{l^2}\right)\left\{\left(1 - \frac{w(l-\lambda)\cos \zeta}{2T_2}\right)^2 - \frac{w^2 l^2}{4T_2^2}\right\},$$

and expanding this to the first power of λ we have

$$c^2 = \frac{T_2^2}{w^2}\sin^2 \zeta\left\{\left(1 - \frac{wl \cos \zeta}{2T^2}\right)^2 - \frac{w^2 l^2}{4T_2^2}\right\}\left(1 + \frac{2\lambda \cos^2 \zeta}{l}\right).$$

Taking for λ the value derived from the second term of the expansion in equation (30), and carrying the factor in λ to the numerator, we see that this correction can be included in the term multiplied by $\cos^2 \zeta$ in the third term of the expansion (30), which now becomes

$$k = l\left[1 - \frac{w^2 l^2 \sin^2 \zeta}{24 T_2^2\left\{\left(1 - \frac{wl \cos \zeta}{2T_2}\right)^2 - \frac{w^2 l^2}{4T_2^2}\right\}} \right.$$
$$\left. + \frac{w^4 l^4 \sin^2 \zeta}{T_2^4\left\{\left(1 - \frac{wl\cos\zeta}{2T_2}\right)^2 - \frac{w^2 l^2}{4T_2^2}\right\}^2}\left(\frac{3}{640} - \frac{\cos^2 \zeta}{384}\right) - \cdots\right]. \quad (31)$$

which is rigorously correct so far as it goes.   Of course if T_1 the lower tension were used we should have to change the minus sign of $\dfrac{wl \cos \zeta}{2T}$ in the denominators into plus.

If we carry both the factors in $\dfrac{w^2 l^2}{T_2}$ in the denominator of the second term to the third we obtain the following :

$$k = l\left[1 - \frac{w^2 l^2 \sin^2 \zeta}{24 T_2^2\left(1 - \frac{wl \cos \zeta}{T_2}\right)} \right.$$
$$\left. - \frac{w^4 l^4 \sin^2 \zeta}{T_2^4\left(1 - \frac{wl \cos \zeta}{T_2}\right)^2}\left(\frac{11}{1920} - \frac{\cos^2 \zeta}{128}\right) - \cdots\right]. \quad (32)$$

from which it will be seen that the sag correction is given with sufficient exactitude for all practical purposes by $\dfrac{w^2 l^3 \sin^2 \zeta}{24 T^2}\left(1 \pm \dfrac{wl \cos \zeta}{T}\right)$ where T is the full end tension, and the upper or lower sign is used according as the tension is

applied to the upper or lower end of the tape. It must be remembered that this gives the difference between the curve and its chord, and if the chord is inclined we must multiply by $\sin \zeta$ again to reduce to the horizontal, but in practice it will be better to do this after applying any further corrections such as for temperature or stretch to k.

We have assumed that the tension observed is the full end tension applied to the tape; and if the tape is used in one bay and the spring balance or weight is applied directly to the end without resting it on any other support, this will be the tension recorded by the balance which will set itself to the angle assumed by the tangent to the tape at its end. When, however, as is generally the case in traverse work, the tape is used supported at several points, part of the full end tension is made up by the reaction of the adjacent support, and the tension recorded by the balance or represented by the weight will in this case be the component of the full tension which is parallel to the chord, and which is with chord horizontal simply T_0. In this last case formula (25) with c put $= \dfrac{T_0}{w}$ gives the sag correction. When the chord is inclined, however, let P_2 be the reaction at the upper end normal to the chord and $\overline{T}_2$ the component of the tension parallel to the chord, then taking moments about the lower support we have $P_2 k = \frac{1}{2} wlk \sin \zeta$, or $P_2 = \frac{1}{2} wl \sin \zeta$, and resolving $\overline{T}_2$ and P_2 horizontally we have

$$T_0 = wc = \overline{T}_2 \sin \zeta - \tfrac{1}{2} wl \sin \zeta \cos \zeta;$$

so that

$$c^2 = \frac{\overline{T}_2^2 \sin^2 \zeta}{w^2} \left(1 - \frac{wl \cos \zeta}{2\overline{T}_2}\right)^2.$$

Substituting this value of c^2 in equation (24) we have

$$k = l\left[1 - \frac{w^2 l^2 \sin^2 \zeta}{24\overline{T}_2^2 \left(1 - \dfrac{wl \cos \zeta}{2\overline{T}_2}\right)^2} \right.$$

$$\left. + \frac{w^4 l^4 \sin^2 \zeta}{\overline{T}_2^4 \left(1 - \dfrac{wl \cos \zeta}{2\overline{T}_2}\right)^4} \left(\frac{3}{640} - \frac{7 \cos^2 \zeta}{1152}\right) - \dots\right]; \quad (33)$$

and if we carry the term in $\dfrac{w^2 l^2 \cos^2 \zeta}{4\overline{T}_2^2}$ in the denominator

of the second to the numerator of the third term, we have

$$k = l \left[1 - \frac{w^2 l^2 \sin^2 \zeta}{24 \mathrm{T}_2^{\,2} \left(1 - \dfrac{wl \cos \zeta}{\mathrm{T}_2} \right)} \right.$$

$$\left. + \frac{w^4 l^4 \sin^2 \zeta}{\mathrm{T}_2^{\,4} \left(1 - \dfrac{wl \cos \zeta}{\mathrm{T}_2} \right)^4} \left(\frac{3}{640} + \frac{5 \cos^2 \zeta}{1152} \right) - \dots \right] \quad (34)$$

If the component at the lower end is used we shall have $\mathrm{T}_1 = \mathrm{T}_2 - wl \cos \zeta$, and the sign of the terms in the denominators by $\cos \zeta$ must be changed.

Also if the tape has several bays in sag it will be seen that the value of T decreases by $wl \cos \zeta$ from bay to bay; so that in calculating the sag correction of them all (supposed equal in length) we have, using the first term of the sag correction from equation (33), a series of the form

$$\frac{w^2 l^3 \sin^2 \zeta}{24 \overline{\mathrm{T}}_n^{\,2}} \left[\frac{1}{\left(1 - \dfrac{wl \cos \zeta}{2 \mathrm{T}_n} \right)^2} \right.$$

$$\left. + \frac{1}{\left(1 - \dfrac{3wl \cos \zeta}{2 \mathrm{T}_n} \right)^2} + \frac{1}{\left(1 - \dfrac{5wl \cos \zeta}{2 \mathrm{T}_n} \right)^2} + \dots \right], \quad (35)$$

where $\overline{\mathrm{T}}_n$ is the observed tension at the upmost support. By expanding these factors and bringing them to the numerator this expression can be put into the form

$$\frac{w^2 l^3 \sin^2 \zeta}{24 \overline{\mathrm{T}}_n^{\,2}} \left\{ n + \frac{n^2 wl \cos \zeta}{\mathrm{T}_n} + \left(n^3 - \frac{n}{4} \right) \frac{w^2 l^2 \cos^2 \zeta}{\mathrm{T}_n^{\,2}} \right\}$$

$$= \frac{n w^2 l^3 \sin^2 \zeta}{24 \overline{\mathrm{T}}_n^{\,2}} \left\{ 1 + \frac{nwl \cos \zeta}{\mathrm{T}_n} + \left(\frac{nwl \cos \zeta}{\overline{\mathrm{T}}_n} \right)^2 \right\} \text{ nearly.} \quad (36)$$

If in the example already considered the tape had been used on a slope of 30°, or $\zeta = 60°$, supported at every 2 chains with a tension of 14 lb. applied to the upper end, we should have total sag correction

$$= \frac{5 \times 0 \cdot 000564^2 \times 1584^3 \times 0 \cdot 866^2}{24 \times 14^2}$$

$$\times \left\{ 1 + \frac{5 \times 0 \cdot 000564 \times 1584}{14 \times 2} + \left(\frac{5 \times 0 \cdot 000564 \times 1584}{14 \times 2} \right)^2 \right\}$$

$$= 1 \cdot 078 \, (1 + 0 \cdot 160 + 0 \cdot 025) = 1 \cdot 194 \text{ inches,}$$

which shows that the third term can usually be neglected.

Thus, so far as the surveyor engaged in traverse work is concerned the sag correction on any slope is given by

$$nl \sin^2 \zeta \left\{ \frac{w^2 l^2}{24\mathrm{T}^2} \left(1 \pm \frac{nwl \cos \zeta}{\mathrm{T}} \right) \right\} ;$$

and the higher the tension the more nearly is this correct. In any case of doubt the next term within the curved brackets is very nearly $-3\left(\dfrac{w^2 l^2}{24\mathrm{T}^2}\right)^2$, which should be increased to $-4\left(\dfrac{w^2 l^2}{24\mathrm{T}_n^2}\right)^2$ if the slope is anywhere near 45°.

Effect of the Elastic Extension.

The effect of the elastic extension of the tape is investigated in the papers above quoted by including it in the equations of equilibrium. As it is an effect of a smaller order than the catenary curve, it is justifiable to assume the tape to have taken the catenary form unstretched and then to add the effect of the stretch. The amount of stretch in any element of length ds is $\dfrac{\mathrm{T}ds}{\mathrm{EA}}$, where T is the tension at that point, E is Young's modulus, and A is the area of the cross section. As the curve is very nearly the catenary, we have $\mathrm{T}=\mathrm{T}_0 \cosh u$, where $u=\dfrac{x}{c}$, x is measured from the vertex of the catenary and $c=\dfrac{\mathrm{T}_0}{w}$. We also have $ds = c \cosh u \, du$.

$$\therefore \quad \frac{\mathrm{T}ds}{\mathrm{EA}} = wc^2 \cosh^2 u \, du;$$

and integrating, we have

$$\int \frac{\mathrm{T}ds}{\mathrm{EA}} = wc^2 \int \cosh^2 u \, du = \frac{wc^2}{\mathrm{EA}} \left(\frac{\sinh 2u}{4} + \frac{u}{2} \right). \quad . \quad (37)$$

If the chord is horizontal we have for the stretch in the whole tape

$$\frac{wc^2}{\mathrm{EA}} \left(\frac{\sinh 2u}{2} + u \right), \text{ and } u = \sinh^{-1} \frac{l}{2c} = \frac{l}{2c} - \frac{l^3}{48c^3} + \dots$$

Expanding this we have

$$\mathrm{Stretch} = \frac{wc^2}{\mathrm{EA}} \left(u + u + \frac{2u^3}{3} + \frac{2u^5}{15} + \dots \right)$$

$$= \frac{wcl}{\mathrm{EA}} \left(1 + \frac{l^2}{24c^2} + \dots \right):$$

and since we have

$$c^2 = \frac{T^2}{w^2} - \frac{l^2}{4} \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

or

$$c = \frac{T}{w}\left(1 - \frac{w^2 l^2}{8 T^2}\right) \text{ nearly,}$$

where T is the end tension, this reduces to

$$\text{Stretch} = \frac{Tl}{EA}\left(1 - \frac{w^2 l^2}{8 T^2}\right)\left(1 + \frac{w^2 l^2}{24 T^2}\right) = \frac{Tl}{EA}\left(1 - \frac{w^2 l^2}{12 T^2}\right). \quad (39)$$

Now $\dfrac{Tl}{EA}$ is the amount by which the tape is stretched when it lies flat, so that $\dfrac{w^2 l^3}{12 EAT}$ is the amount by which it contracts in length if it has been standardized flat under an end tension T, and is then used in catenary under the same end tension, the contraction being due to a diminution in the mean tension owing to the curvature and having nothing to do with the sag correction.

Professor Maclaurin in his paper compares the stretch correction with the stiffness correction, and finds the former $= 1 \cdot 757$ inch ; but he assumes that the tape has been standardized under no tension, *i. e.* he uses the expression $\dfrac{wcl}{EA}$. If the tape in question had been standardized flat under 14 lb. tension the shortening when used horizontally in catenary owing to decrease of stretch would be

$$\frac{0 \cdot 000564^2 \times 7920^3 \times 8 \times 60}{12 \times 3 \times 10^7 \times 14} = 0 \cdot 0150 \text{ inch;}$$

which we see is just about the same as the value found for the stiffness correction with constrained ends, viz. $0 \cdot 0123$ inch; and as these two corrections are of opposite sign they mutually destroy one another in this case.

Considering the stretch correction when the tape is on a slope, we have

$$\int_{u_1}^{u_2} T ds = \frac{T_0 c}{2}\left(\frac{\sinh 2u_2}{2} - \frac{\sinh 2u_1}{2} + u_2 - u_1\right)$$

$$= \frac{T_0 c}{2}\left(\cosh (u_2 + u_1) \sinh (u_2 - u_1) + u_2 - u_1\right)$$

$$= \frac{T_0 c}{2}\left\{2 \cosh^2 \frac{(u_2 + u_1)}{2} \, 2 \sinh\frac{(u_2 - u_1)}{2} \cosh \frac{(u_2 - u_1)}{2}\right.$$

$$\left. - \sinh (u_2 - u_1) + u_2 - u_1\right\}$$

$$= \frac{T_0 c}{2}\left\{2 \cosh \frac{u_2 + u_1}{2} \cosh \frac{u_2 - u_1}{2} \, 2 \cosh \frac{u_2 + u_1}{2} \sinh \frac{u_2 - u_1}{2}\right.$$

$$\left. - \frac{(u_2 - u_1)^3}{3.2} - \cdots\right\}$$

Now

$$2 \cosh \frac{u_2 + u_1}{2} \cosh \frac{u_2 - u_1}{2} = \cosh u_2 + \cosh u_1 = \frac{T_2 + T_1}{T_0},$$

and

$$2 \cosh \frac{u_2 + u_1}{2} \sinh \frac{u_2 - u_1}{2} = \sinh u_2 - \sinh u_1 = \frac{l}{c};$$

∴ Stretch

$$= \frac{T_0 c}{2EA} \left\{ \frac{l}{c} \cdot \frac{T_2 + T_1}{T_0} - \frac{(u_2 - u_1)^3}{6} - 3\frac{(u_2 - u_1)^5}{40} - \dots \right\} \quad . \quad (40)$$

$$= l \cdot \frac{T_2 + T_1}{2EA} - \frac{wc^2(u_2 - u_1)^3}{12EA} - \dots ;$$

but

$$u_2 - u_1 = \frac{x_2 - x_1}{c} = \frac{l \sin \zeta}{c}, \text{ nearly,}$$

and

$$T_1 = T_2 - wh = T_2 - wl \cos \zeta, \text{ nearly;}$$

also

$$c = \sin \zeta \frac{T_2}{w}, \text{ nearly;}$$

∴ Stretch

$$= \frac{T_2 l}{EA} \left\{ 1 - \frac{wl \cos \zeta}{2T_2} - \frac{w^2 l^2 \sin^2 \zeta}{12T_2^2} \dots \right\} \text{ nearly.} \quad . \quad (41)$$

This of course reduces to the expression (39) when $\zeta = 90°$; and it will be seen that the second term rapidly becomes of more importance than the third. In the example considered these two terms are equal for $\zeta = 86° 50'$. The correction to be applied therefore to a measured distance when the tape has been standardized on the flat under T_2 lb., and is used on a slope inclined ζ to the vertical, is

$$- \left(\frac{wl^2 \cos \zeta}{2EA} + \frac{w^2 l^3 \sin^2 \zeta}{12EAT_2} \right).$$

The first term is simply the stretch caused by the component of the tape's own weight, and if the tension at the lower end is used its sign must be changed. When the tape hangs in several bays the above expression must be multiplied by the number of bays to obtain the full correction.

If the mean tension were kept constant as indicated in the paper by Professor and Captain Henrici, the first term of the correction would vanish. This would mean, however, adjusting the tensions for every change of slope, which in

practice would be a rather tedious operation. If also the tape were standardized in catenary, the third term would be replaced by

$$\frac{w^2 l^3}{12\,\text{EAT}_2}\,(1 - \sin^2 \zeta) = \frac{w^2 l^3 \cos^2 \zeta}{12\,\text{EAT}_2},$$

a very small quantity indeed, as pointed out and exemplified in a different form in the paper just quoted.

Effect on the Sag Correction of using Tapes of different Density.

In the standard traverse work of the Malay States Survey Department, the tape used is of steel or invar wire of rectangular section about $\frac{1}{16}$ inch wide and $\frac{1}{50}$ inch thick, weighing about 5·1 oz. Av. per chain of 66 feet. This wire can be obtained from Messrs. J. Chesterman & Co., Sheffield, in continuous lengths of 1000 feet or more. It was customary to obtain it in lengths of about 10 chains or 660 feet, and to mark it off locally at every chain standard when flat at about 90° F. (the mean temperature of working) with 20 lb. tension. In order to obtain the odd linkage of his traverse lines the surveyor was also supplied with a steel box tape 66 or 100 feet long, with divisions etched on it to hundredths of links standard, also at about 90° F. under 20 lb. tension. This box tape could be attached to a loop at the end of the $\frac{1}{16}$ tape by a split hook; and it was arranged in marking off the latter that the divisions on the box tape should read correctly. Obviously it was desirable that the box tape should have the same density as the $\frac{1}{16}$ tape; but it was not possible to show the etching on the former clearly with a less width than $\frac{1}{4}$ inch. The thickness was reduced somewhat to counteract this, but could not be reduced with safety to give a less density than 7·3 oz. per chain. The question having arisen as to whether this extra density at the end of the series could appreciably affect the sag correction of the $\frac{1}{16}$ tape for which tables had been calculated, the writer was led to investigate the question mathematically; and as he has not seen the result published anywhere, he appends it to this paper in case it may be of use or interest to other surveyors.

In the case in point the denser tape is at one end of the series, and this is the case the writer first solved; but he afterwards worked out the more general case where the denser tape may be anywhere in the series; and as this includes the other the working out of it only will be given.

(Fig. 4.) Let l be the whole length of the tapes in sag, the chord being supposed horizontal, w be the weight per unit of length of the lighter tape, w' the excess weight per unit of length of the heavier over the lighter, rl the fraction of
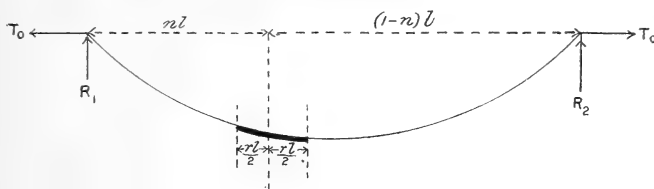
FIG. 4.

the whole length covered by the heavier, and nl, $(1-r)l$ the distances from either end to the middle of the heavier tape, R_1 and R_2 the vertical reactions, and T_0 the horizontal component of the tension.

Taking moments about the R_2 support, we have

$$R_1 l = \frac{wl^2}{2} + w'rl(1-r)l, \quad \text{or} \quad R_1 = \frac{wl}{2} + w'r(1-r)l.$$

We also have the following moment equations for the several sections:—

$$T_0 y = R_1 x - \frac{wx^2}{2}, \quad \text{from } x=0 \text{ to } x=nl-\tfrac{1}{2}rl;$$

$$T_0 y = R_1 x - \frac{wx^2}{2} - \frac{w'}{2}(x-nl+\tfrac{1}{2}rl)^2, \quad \text{from } x=nl-\tfrac{1}{2}rl \text{ to } x=nl+\tfrac{1}{2}rl;$$

$$T_0 y = R_1 x - \frac{wx^2}{2} - w'rl(x-nl), \quad \text{from } x=nl+\tfrac{1}{2}rl \text{ to } x=l.$$

Therefore

$$T_0 \frac{dy}{dx} = R_1 - wx, \quad \text{from } x=0 \text{ to } x=(n-\tfrac{1}{2}r)l;$$

$$T_0 \frac{dy}{dx} = R_1 - wx - w'(x-nl+\tfrac{1}{2}rl), \quad \text{from } x=(n-\tfrac{1}{2}r)l \text{ to } x=(n+\tfrac{1}{2}r)l;$$

$$T_0 \frac{dy}{dx} = R_1 - wx - w'rl, \quad \text{from } x=(n+\tfrac{1}{2}r)l \text{ to } x=l.$$

Therefore $\quad T_0^2 \int_0^l \left(\frac{dy}{dx}\right)^2 dx = 2T_0^2 \times \text{sag correction} =$

$$\int_0^l (R_1-wx)^2 dx - 2w' \int_{(r-\frac{1}{2}r)l}^{(r+\frac{1}{2}r)l} (R_1-wx)(x-nl+\tfrac{1}{2}rl)dx + w'^2 \int_{(n-\frac{1}{2}r)l}^{(n+\frac{1}{2}r)l} (x-nl+\tfrac{1}{2}rl)^2 dx$$

$$- 2w'rl \int_{(n+\frac{1}{2}r)l}^{l} (R_1-wx)dx + w'^2 r^2 l^2 \int \, dx.$$

The integrals are rather tiresome to evaluate, but many terms cancel out, and the following fairly simple result is obtained for the Sag Correction:

$$\frac{l^3}{24T_0^2}\left[w^2 + 12ww'r\left\{n(1-n)-\frac{r^2}{12}\right\} + 12w'^2r^2\left\{n(1-n)-\frac{r}{6}\right\}\right]. \quad (42)$$

If we make $n=\frac{r}{2}$, we have the case of heavier tape at one end of the series, and the formula reduces to

$$\frac{l^3}{24T_0^2}\left[w^2 + 2ww'(3r^2-2r^3)+w'^2r^2(4r-3r^2)\right]. \quad (43)$$

If we make $r=1$, we get simply $\dfrac{l^3(w+w')^2}{24T_0^2}$, as we should.

If in equation (42) we write $w'rl=$ W the whole extra weight of the heavier tape and then make the r's within the brackets vanish, we obtain the formula for the effect of a concentrated weight W attached to the tape in any position, thus

$$\frac{l}{24T_0^2}\left[w^2l^2 + 12wlWn(1-n)+12W^2n(1-n)\right], \quad (44)$$

which of course is greatest for $n=\frac{1}{2}$, or weight at centre of tape. Putting $w=0$, we see the effect of a concentrated weight at the centre is 3 times as great as the effect of the same weight uniformly distributed.

Returning to equation (43), we see that the error introduced by using a slightly heavier tape at the end of the series is as a fraction of the whole length in sag approximately $\dfrac{l^2ww'r^2}{4T_0^2}$. The maximum value of this error occurs when the whole chain of heavier tape is in use, so that when $l=2$ chains $r=\frac{1}{2}$, $l=3$ chains $r=\frac{1}{3}$, and so on. Thus $l^2r^2=$ constant $=1$, and as in the case for which the investigation was made $w=5\cdot1$ oz., $w'=2\cdot2$ oz., $T_0=20$ lb., we have the above fraction $= \dfrac{5\cdot1\times2\cdot2}{4\times20^2\times16^2}=\dfrac{11\cdot2}{409,600}$, say 1 in 40,000. The *average* effect occurs when only half the heavier tape is in use and is $\frac{1}{4}$ the above ratio, or about 1 in 160,000. As an accuracy of only about 1 in 30,000 was aimed at in the traverse work on which these tapes were used, this correction was therefore negligible.

Formula (44) might be of use when for some purpose an attachment is made to the tape such as a thermometer to obtain the temperature at a certain point; and in this connexion the writer worked out in a similar way the effect of a

number of equal concentrated loads each $=\mathrm{W}$ spaced at equal distances along the tape in sag. The result is Sag Correction =

$$\frac{l}{24\mathrm{T}_0^2}\left[w^2l^2 + 2\mathrm{W}wl\frac{(m^2-1)}{m} + \mathrm{W}^2(m^2-1)\right], \quad . \quad (45)$$

where m is the number of spaces = number of loads $+1$. If we make $m=2$, we obtain

$$\frac{l}{24\mathrm{T}_0^2}\left[w^2l^2 + 3\mathrm{W}wl + 3\mathrm{W}^2\right],$$

the same as making $n=\frac{1}{2}$ in formula (44).

In order to test these formulæ the writer had some experiments made which were carried out by Mr. W. A. Wallace, a Surveyor of the Trigonometrical Survey Department of the Malay States. A $\frac{1}{16}$ tape 7 chains long was stretched in sag under 20 lb. tension, and the movement of one end was noted when a weight of 1 lb. was placed at successive intervals of 1 chain along the tape, and also when 1 lb. weights were placed at each chain. The tape weighed 5·1 oz. per chain of 66 feet. The following are the results giving the differences between observed and calculated effects :—

Position of Weight.	Movement observed.	Movement calculated.	Difference, obs.—calc.
W at 1 chain	0·357 link	0·346 link	+0·013 link
„ 2 chains.....	0·521 „	0·577 „	−0·056 „
„ 3 „	0·710 „	0·692 „	+0·018 „
„ 4 „	0·664 „	0·692 „	− 0 028 „
„ 5 „	0·536 „	0·577 „	−0·041 „
„ 1 to 6 chains incl...	5·641 „	5·731 „	−0·090 „

The differences are greater than the writer would have expected, and may be due to differences of elasticity in the tape which has of course been assumed to be homogeneous. Mr. Wallace was not satisfied with the conditions under which the tests were made. Allowance was made for change of temperature, but he notes that there were passing clouds which may have affected the temperature of the tape more than the thermometers. There was also a slight breeze, and it was intended to repeat the experiment under more favourable

conditions, but unfortunately this intention was not carried out. The agreement, however, is close enough to show that no blunder has been made in working out the theory.

The writer also made experiments to test the ordinary sag formula while he was engaged in measuring in 1900 a base-line with a $\frac{1}{4}$-inch tape of about the same thickness $\frac{1}{50}$ inch and 500 feet long. This was supported during the measurement at intervals of 50 feet, and stretched by an end tension of 20 lb. In the tests supports were placed also at every 5 feet, and the movement of one end of the tape was observed when it was supported at these and various other intervals. The writer has not the actual figures at hand, but the agreement, speaking from memory, was nearly perfect between observation and calculation, the difference between a change from 5 to 50 feet intervals in the supports being about $\frac{1}{100}$ inch. Such a test includes of course the effect of bending.

It was for long the writer's desire to test the sag formulæ on slopes of high magnitude, say 45° to 60°, with a good length of tape in sag and with various tensions, in order to see practically where the limits of applicability of the formulæ lie, but unfortunately he was unable to carry out this intention before retiring from the Malay States Survey. He gives the following sketch of how he intended to proceed in case any other surveyor may have the desire and opportunity of making the tests.

The tests should be made with as long a tape as possible; and as wire can be obtained in continuous lengths of 1000 feet and more, there is no difficulty in getting a good long continuous and presumably homogeneous tape. The chief difficulty would be in finding a site, which would have to include either a tower or precipitous hill or cliff, say 500 feet above a plain where base-lines could be measured. Two or three base-lines should be measured on this plain giving slopes from 45° to 60° from their ends with a point on the summit; and it would be well to have each in two sections, to give a check in the calculated distances to the latter. The base-lines should be measured with the tape to be used on the slopes, and the station on the summit carefully triangulated into. Very careful vertical angles should be observed reciprocally if possible, so that the direct chord distances from base stations to summit could be calculated with precision, refraction being eliminated as far as possible. These calculated distances could then be compared with those given by the tape used on the slope from base to summit directly, and with various tensions. As there should be no interference

from wind, and as the temperature should be as uniform as possible, probably the best site could be found in some tropical country with steep limestone cliffs sheltered from winds by jungle; and it would be advisable to use an invar wire. The actual form of the tape could be studied by attaching light paper marks to it at known intervals to which reciprocal vertical angles could be observed by theodolites mounted at the upper and lower ends. The writer concludes by hoping that some reader may have the will and opportunity to make such tests.

University Observatory, Oxford.
June 1914.

XII. *Note on the Theory of the Metallic State.* *By* F. A. LINDEMANN, *Ph.D.*[*]

THE outstanding physical properties of metals have hitherto been attributed to the presence of a number of so-called free electrons in the interstices between the atoms. These electrons, which are supposed to behave like a perfect gas, may be made to explain most electrical phenomena in metals with fair accuracy.

The conduction of electricity is considered to be due to a drift of electrons caused by the field. The electrical resistance is accounted for by the collisions of the electrons with the atoms, and Ohm's law is explained by the large number of collisions in unit time. The resistance may be expected to change if an alternating current of such a high frequency is induced that there are no longer a large number of collisions during one phase. This has been observed to be the case if currents of about 10^{14} periods per second are induced, as is done when infra-red light is reflected. From this one may conclude that an electron must undergo at least 10^{14} collisions per second. As the resistance is $\dfrac{2m}{Ne^2 t}$, where m is the mass, N the number per cm.[3], e the charge, and t the time between the two collisions, a lower limit for N may be determined. Putting in the known values one finds about three times as many electrons as atoms. This is approximately the same number as one finds from a consideration of the dispersion of metals.

Various theories have been proposed to explain the fact that the electrical resistance of a metal at different temperatures is approximately proportional to the heat-content.

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[*] Communicated by Prof. J. W. Nicholson.

The latest and most elaborate assume the electrons to have certain definite velocities which are independent of the temperature [*]. Like Planck's zero-point energy (Nullpunktsenergie) this motion cannot be interchanged or observed. The variation of the resistance with the temperature is attributed to the change in the mean free path due to the change in the amplitude of the atom's oscillations. These theories do not account for the supra-conductivity at temperatures below $3°$ absolute.

Conduction of heat in metals is usually assumed to take place analogously to in a gas, the electrons taking the place of the gas molecules. The formula found is $\lambda = \dfrac{\mathrm{N}mcl}{3}\gamma$, l being the mean free path, c the velocity, and γ the specific heat of 1 gram of electrons. Comparing this with the expression for the electrical conductivity $\sigma = \dfrac{\mathrm{N}e^2t}{2m} = \dfrac{\mathrm{N}e^2l}{2mc}$ one finds $\dfrac{\lambda}{c} = \dfrac{m^2c^2}{6e^2}\gamma$. This reduces to the Wiedemann-Franz law if one assumes the atomic heats (and therefore also the speed of the electrons) to be independent of the metal. If one supposes the law of the equipartition of energy to hold, γ must be $\dfrac{\mathrm{M}}{m}\cdot\dfrac{3\mathrm{R}}{2}$ where M is the mass of an atom of hydrogen, m the mass of an electron, and $\dfrac{mc^2}{2}$ must be $\dfrac{3\mathrm{R}T}{2n}$ where n is the number of atoms in a gram-atom, and T the absolute temperature. Thus $\dfrac{\lambda}{\sigma}$ reduces to $\dfrac{3\mathrm{M}\mathrm{R}^2T}{4ne^2}$ or $\dfrac{3}{4}\dfrac{\mathrm{R}^2}{e^2n^2}T$ as $\mathrm{M} = \dfrac{1}{n}$. This value is in very fair agreement with the constant of the Wiedemann-Franz law, and the variation of the constant with the absolute temperature is in accordance with the facts.

It is unnecessary to go into the various theories that have been put forward to explain the various secondary phenomena, such as the Peltier effect, the Hall effect, the Thomson effect, the Richardson effect, and so on. Each has necessitated secondary hypotheses, and none of them is very convincing. It is sufficient to point out that the main points enumerated above are in absolute contradiction with one another or with the facts. The most obvious difficulty, of course, is the

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[*] W. Wien, *Berl. Ber.* 6. ii. 1913 ; W. H. Keesom, *Phys. ZS.* xiv. p. 670 (1913).

question of the atomic heat of metals. Measurement shows that there cannot be more than one free electron per hundred atoms if the electron obeys the law of the equipartition of energy, for the atomic heat of metals corresponds in every respect to that of metalloids. As shown above, the conductivity leads to the conclusion that there are more free electrons than atoms. If one gives up the law of the equipartition of energy, which at first sight seems the simplest way out of the difficulty, one cannot explain the conduction of heat and the Wiedemann-Franz constant. Thus the electrical conductivity leads to a large number of free electrons. Its temperature coefficient leads to no specific heat. But the heat conduction cannot be explained except by a normal specific heat. Again, the measured heat capacities are incompatible with a large number of electrons or with a normal specific heat.

The expression free electron, suggesting, and intending to suggest, an electron normally not under the action of any force, like an atom in a monatomic gas, might almost be called a contradiction in terms. If one assumes that the electrons are not attracted by the ions (and this assumption is essential, for otherwise they would recombine with them), the forces between the electrons themselves will prevent their being free in the true sense. Indeed, the force preventing one electron from moving between two others at a distance of $3 \cdot 10^{-8}$ cm., corresponding to about one electron per atom, is so great that the equipartition energy $\frac{3R}{2n}$T could only shift it by about 1/20 of the distance apart.

These figures may be modified, of course, by assuming the ions at a distance to attract the electrons, and some such supposition must be made, as the electrons would otherwise not remain in the metal at all. But the forces exerted by the neighbouring electrons whose repulsion is not neutralized are sufficient to prevent any similarity to a gas. The hypothesis put forward in this paper is, that far from forming a sort of perfect gas the electrons in a metal may be looked upon as a perfect solid.

This conception would appear not to lead to any serious contradictions, and even to supply an explanation for one or two phenomena which the old theory hardly touches upon.

The following assumptions would appear to be necessary to explain the facts :—

1. Though attracted, according to the inverse square law, by ions at distances sensibly greater than the atom's radius, the electrons are repelled at distances less than r_0, by a force

equal to $kf(r)$. This hypothesis, though not explicitly stated in the ordinary electron theory, is accepted in its main outlines, for if an electron were attracted with a force $\frac{e^2}{r^2}$, the small kinetic energy attributed to it, $\frac{3R}{2n}$ T, could never enable it to dissociate from the ion. The hypothesis seems to be rendered fairly plausible by the experiments on the reflexion of electrons by atoms described by Franck and Hertz [*].

2. The number of electrons per cm.³, N, the dielectric constant of the ions D and the constant k of the repulsive force $kf(r)$ are such that $\phi(N, k) \sim \psi(N, D)$. The functions ϕ and ψ will be defined later on. The equation probably reduces to $\frac{N}{k^{1/2}D^{3/2}} = $ const., or if D is constant, to $N \sim \sqrt{k}$. This hypothesis is introduced to account for Wiedemann-Franz's law.

We need only consider crystals for the time being, as all metals consist of an agglomeration of, often microscopic, crystals. A metal crystal would consist of two interleaved space-lattices, one consisting of atoms or ions, one of electrons.

To work out the exact mathematical consequences of this conception will be a matter of great difficulty. This paper will be confined to a general review of the various phenomena and an outline of the way this hypothesis might explain them.

Electric conduction.—If a metal crystal is brought into an electric field the electron space-lattice will shift in respect to the atoms until the attraction of the more distant ions counterbalances the force exerted by the field. If a source of electrons is brought into contact with the one end and if they can flow out at the other, *e. g.* if the crystal is connected to the two poles of a battery, the attraction of the more distant ions will be counterbalanced by the repulsion of the inflowing electrons, and the electron space-lattice will move continuously through the atomic space-lattice. In other words, the electron space-lattice or crystal may be said to melt at the one end and fresh layers may be said to freeze on at the other end when a current flows. If the distance to which the repulsive force of the ions extends, r_0, is less than $\frac{r}{2}$, half the distance between the centres of the atoms, the

electron space-lattice can move unimpeded through the atom space-lattice, as long as the atoms are at rest or as long as their vibrations do not extend to an amplitude $\dfrac{r - 2r_0}{2}$. This would correspond to the supra-conductive state described by Kamerlingh-Onnes as occurring in pure metals at temperatures below about $3°$ [*]. If, however, the metal is not pure this supra-conductive state can never be attained, for the regularity of the original atomic space-lattice is destroyed by the other atoms embedded in it, and the electron space-lattice would always encounter a comparatively large resistance which would be independent of the temperature. This corresponds to the formula $W = W_0 + f(T)$ discovered by Nernst [†], in which the resistance W is equal to the resistance $f(T)$ of the pure metal plus a constant W_0 depending upon the impurities.

To return to the pure metal, as the temperature increases the amplitude of the atomic vibrations increases and the electron space-lattice can no longer pass without resistance.

Every electron will have to pass through the spheres of repulsion on its path and will transfer the kinetic energy gained from the electric field to the atoms. The mean velocity of the electron space-lattice v is obviously proportional to the current as the number is constant ; the mean velocity imparted to one electron by the field is $\dfrac{ex}{2m}\tau$, where τ is the time between two collisions with a repulsive sphere. $\tau = \dfrac{1}{\nu}$, whilst the electron is in the immediate neighbourhood of an atom if ν' is the atom's frequency. During the rest of the time $\tau = \dfrac{d}{v}$, where d is the distance during which the electron is further removed from the atom's centre than $r_0 + A$, A being the atom's amplitude. Now, as we always have a very large number of electrons in any observable current, there are always a large number of electrons within the distance $r_0 + A$ of an atom, consequently the time during which the entire electron space-lattice can move unimpeded is infinitesimal. It follows that Ohm's law holds good as the current $a \backsim v \backsim x$. Further, it may be expected to hold for any current whose duration is of the order $\dfrac{1}{\nu'}$, or greater.

* Leiden Communications, 124 C.
† *Berl. Ber.* ii. p. 23 (1911).

The calculation of the variation of the electrical resistance with the temperature cannot be attempted here.   It depends obviously upon the amplitude of the atomic vibrations and upon the force acting upon the electrons whilst they are within the sphere of repulsion.   As, according to Debye, there are vibrations of almost every frequency less than ν_m, and as all their amplitudes may vary, it will certainly be very difficult to take an average of all the probable forces acting upon the electron space-lattice.   We may take it, however, that there exists a law of force $kf(r)$ which entails a resistance proportional to the square of the amplitude A, *i. e.* proportional to the energy E as $A^2 = \dfrac{E}{\alpha}$, if α is the quasi-elastic force holding the atoms in position.   As has been shown, α is roughly proportional to N, the number of electrons per cm.^{3} *.   Therefore the resistance is a function of N and k, say $\phi(N, k)E$.   The dimensions would seem to lead to the formula $\dfrac{1}{\sigma} = \dfrac{\rho^{1/2}}{N^{2/3}k^{1,2}}E$, ρ being the density of the electron space-lattice.   As ρ, N and k are independent of the temperature, the resistance is thus in accord with the experimental facts.

This proportionality of the resistance to the temperature only holds good of course for pure metals.   In alloys consisting of metals which do not form mixed crystals, *i. e.* which consist of an agglomeration of pure crystals, the resistance might be expected to be the sum of the resistance of the components and the temperature coefficient would be normal. In other alloys the homogeneity of the space-lattice would be disturbed and the resistance would be larger.   The temperature coefficient would probably be smaller, for the heat-motion might in some cases render the passage of the electrons more easy, as the interspersed atoms which are in the way might be moved into a more favourable position. Somewhat similar phenomena may be expected in a liquid metal, whose conductivity should be considerably less than it is in the solid state.

Conduction of heat.—Debye has shown that a homogeneous space-lattice would have apparently infinite heat conductivity †.   This diminishes the less homogeneous the space-lattice becomes.   Debye's theory explains Eucken's apparently paradoxical experimental results on heat con-

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* *Verh. d. d. Phys. Ges.* xiii. 24. pp. 1107 & 1117 (1911).

† 'Vorträge über die kinetische Theorie der Materie und Elektricität' (Teubner), 1914.

ductivity of crystals at low temperatures [*], namely, that the reciprocal of the heat conductivity, the thermic resistance, is approximately proportional to the temperature. According to Debye the heat is transported in the form of elastic waves. These are scattered by inhomogeneity in the elastic constants of the space-lattice, caused by variations in density due to heat-motion. If a metal is composed of two interleaved space-lattices, as assumed in this paper, its measured heat conductivity will be the sum of the conductivity of the atomic space-lattice and that of the electron space-lattice. At ordinary temperatures the conductivity of the atomic space-lattice may be neglected, as it will be of the same order as that of a crystal. The conductivity of the electron space-lattice will be comparatively very great, for it corresponds to a crystal at a very low temperature. Now the formula for the conduction of heat developed by Debye is only valid for temperatures of the order $T > \beta \nu_m$, ν_m being the limiting frequency. The electron space-lattice will have a very high limiting frequency according to Debye's formula $\nu_m = \left(\dfrac{9}{4\pi} \right)^{1/3} \dfrac{N^{1/3}}{\rho^{1/2} \kappa^{1/2}}$, on account of its small mass and comparatively small compressibility. For N one can put $\dfrac{pn}{v}$, p being the proportion of atoms dissociated ; ρ, the density, is $Nm = \dfrac{pmn}{v}$, m being the mass of an electron, whilst the compressibility κ depends upon N and the dielectric constant. Now there is no reason why, if one atom expels an electron, all the others should not do the same ; therefore p is probably one, perhaps two or more. In this case κ is of the same order as it is for the solid [†], though its exact value depends upon the distance at which the attraction of the ions becomes noticeable and upon the dielectric constant D of the material. Therefore ν_m is of the order $\sqrt{\dfrac{M}{m}} \nu'_m$, M being the mass of the atom and ν'_m the limiting frequency of the atomic space-lattice [‡]. As $\sqrt{\dfrac{M}{m}}$ is between 100 and 600, the electron space-lattice at 300° corresponds to the

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[*] *Ann. d. Phys.* (4) xxxiv. p. 185 (1911).

[†] According to Haber's empirical formula, it should be exactly the same (vide *Verh. d. d. Phys. Ges.* xiii. 24. p. 1117 (1911)).

[‡] For the sake of simplicity only the compressibility has been taken into account. In other words, the velocity of a transversal wave is assumed proportional to the velocity of a longitudinal wave.

metal at $3°$ to $1/2°$ Abs. In this region we cannot apply Debye's formula for the conduction of heat. We can only conclude from his reasoning that it must be large. Only an exact theory could give some idea as to his "free path" l, which he defined as the distance in which the energy of the elastic waves is diminished to $\frac{1}{e^{\text{th}}}$ part. He finds the heat conductivity $\lambda = \frac{\rho q \gamma}{4} l$, q being the velocity of sound $\frac{1}{\sqrt{\rho \kappa}}$, γ the specific heat. As has been or will be shown, ρ, κ, and γ depend upon N and D, l can only depend upon the number of layers of atoms per cm. $\smile v^{-1/3}$ or upon N and probably T. Therefore $\lambda = f(\text{N, D, T})$. Although we lack an exact theory for the conductivity of a crystal at very low temperatures, we can conclude from the measured conductivity of the diamond that it does not vary with the temperature. Therefore λ reduces to $\psi(\text{N, D})$, and this theory gives the law of Wiedemann-Franz, $\frac{\lambda}{\sigma} = \text{E const.}$, if $\lambda = \psi(\text{N, D}) \smile \phi(\text{N}, k) = \frac{\sigma}{\text{E}}$. A consideration of the dimensions appears to lead to the equation $\lambda \smile \frac{1}{\text{N}^{1/3}\rho^{1/2}\kappa^{3/2}}$.

If this be true, $\frac{\lambda}{\sigma} = \frac{1}{\text{N} k^{1/2}\kappa^{3/2}}$E. This assumption is of course simply introduced to show that the observed proportionality of electric and heat conductivities is not inconsistent with the electron space-lattice hypothesis. The suggested theory does not pretend to predict this law as the old theory does; but, on the other hand, it would not seem to lead to the absolute contradictions for which the old theory is noted. If κ is of the form $\frac{\text{D}}{\text{N}^{4/3}}$, $\frac{\lambda}{\sigma}$ reduces to $\frac{\text{N}}{k^{1/2}\text{D}^{3/2}}$. Thus supposing, for instance, D to be equal for all metals, $k \smile \text{N}^2$ would lead to the law of Wiedemann-Franz. As in the case of the electrical conductivity, impurities should produce inhomogeneity of the space-lattice and thereby diminish the heat-conductivity.

Specific heat.—At emphasized above, the question of the specific heat of the electrons has been the chief stumbling-block of the old theory. The argument which leads to the difficulty, namely, that as the electrons conduct heat so well they must have a large heat-capacity, is sound only as long as the electrons behave like a gas. If they form a solid, on the other hand, the converse is nearer the truth.

There are analogies, as stated above, in the conduction of

heat by a diamond at 20° Abs. Its conductivity is almost as great as that of copper, although its specific heat is negligible. The specific heat of the electron space-lattice may probably be calculated fairly accurately from Debye's formula, which has proved so successful in the case of solids *. The atomic heat is

$$ c_v = 3\mathrm{R} \left[\frac{12T^3}{(\beta\nu_m)^3} \int_0^{\frac{\beta\nu_m}{T}} \frac{\xi^3 d\xi}{e^\xi - 1} - \frac{3\beta\nu_m}{e^{\frac{\beta\nu_m}{T}} - 1} \right] \text{ if } \nu_m = \left(\frac{9}{4\pi}\right)^{1/3} \frac{\mathrm{N}^{1/3}}{\rho^{1/2}\kappa^{1/2}} $$

In our case, as shown above, the velocity of sound, $\dfrac{1}{\rho^{1/2}\kappa^{1/2}}$, is very large †, on account of the small density, so that c_v reduces to the form $\dfrac{12\pi^4}{5} \mathrm{R} \dfrac{T^3}{(\beta\nu_m)^3}$, and the specific heat of the electrons is well below the limits of measurement. Taking one electron per atom and κ equal to the compressibility of silver, for instance, ν_m would be

$$ 436 . 4{\cdot}42 . 10^{12} = 1{\cdot}93 . 10^{15} \quad \text{or} \quad \beta\nu_m = 94000. $$

Thus the atomic heat at 300° would be $1{\cdot}51 . 10^{-5}$ cal. or the specific heat $\gamma = 0{\cdot}266$ cal.

This explains, too, why those phenomena which depend upon the energy-content of the electrons are so minute.

Contact potential.—The electrons in the metal will have many points of similarity with a solution in spite of forming a space-lattice. Their mutual repulsion must be counterbalanced by the attraction of the more distant ions. We thus have an analogous phenomenon to the internal pressure in liquids in the theories of van der Waals and Reinganum, or to the osmotic pressure in solutions.

If two metals are placed in contact, the electrons will flow from the metal with higher internal pressure into that with lower until the potential difference balances the difference in pressure.

Other things being equal, the work necessary to remove an electron will be inversely proportional to the cube root of the atomic volume. Hence, in general, the metals with large atomic volumes, such as the alkali metals, will become

* *Ann. d. Phys.* (4) xxxix. p. 789 (1912).

† It is interesting to find that the velocity calculated by this formula is of the order $10^8 \frac{\text{cm.}}{\text{sec.}}$, which is about the value found for the transmission of energy through a cable. It is difficult to see how these high velocities can be explained on the old electron theory, for a wave can never travel faster in a gas than the velocity of the molecules.

positively charged on being placed in contact with a metal of smaller atomic volume. Similarly, their electrons will go into solution more easily than those of other metals, *i.e.* they are electropositive.

Thermoelectric effect.—The internal pressure of the electron space-lattice will obviously depend upon the temperature mainly on account of the thermal expansion of the metal. But it will not necessarily change with the temperature according to the same formula in different metals. Therefore if a ring is formed of two different metals and the two junctions kept at different temperatures, the difference of the internal pressures at the one junction will not necessarily be counterbalanced by the difference at the other junction. In all cases in which the pressure differences are not equal and opposite, a current will flow in the ring and continue flowing as long as the temperatures of the two junctions are kept constant.

In a metal in a state of strain, the relative positions of the atoms and electrons would be slightly different from the positions in the unstrained state. This would lead to changes in the elastic coefficients of the electron space-lattice, and thus probably to thermoelectric effects between parts under different stresses.

Peltier Effect.—The electron space-lattice in a metal has a certain stability, and may consequently be expected to have a certain latent heat of fusion. The passing of electricity from one metal to another entails the melting of the electron-crystal in the metal connected to the negative pole and the solidifying in the other metal. The difference in the different latent heats of fusion will be absorbed or liberated at the junction according to whether the current flows from the metal whose electron space-lattice has a large latent heat of fusion to the one whose latent heat of fusion is smaller or *vice versa*.

Richardson Effect.—Just as any other crystal, a crystal composed of electrons must have a certain vapour pressure. As in the case of solids, this may be expressed by a formula of the form $Ae^{-\frac{B}{T}}T^c$, a similar formula to that found already by Richardson.

Reflexion.—As observed above, the resistance of a metal should be independent of the period of the current if this is greater than v'_m the period of the atoms. The resistance opposed to the more rapid alternations of the currents induced by reflexion of shorter waves than the "remaining rays" must depend upon the number of electrons involved.

In addition to this the electron space-lattice may be expected to have a large number of proper frequencies, which will modify the coefficient of reflexion. The proper frequencies must actually become most numerous in the region in which the deviations really commence. As will be shown, their number should be $\dfrac{9N}{\nu_m{}^3}\nu^2\,d\nu$.

Putting in the values assumed above this is of the order $\dfrac{2 \cdot 10^{33}}{\lambda^4}\,d\lambda$, λ being measured in Ångström units, 10^{-10} metre.

Thus for waves 1 mm. long there would still be $2 \cdot 10^5$ frequencies per tenth-metre. Planck's infinite number of resonators of different frequencies may thus have a physical meaning, though in our case the number is confined to $3N$, and the frequencies are less than ν_m.

Photoelectric Effect.—One would need special assumptions to calculate the proper frequencies of the electron space-lattice as Born and Karman did for atomic space-lattices. Fortunately, however, we can use the method which Debye proved was permissible as a first approximation for atomic space-lattices, namely that used by Rayleigh in developing the first radiation formula. According to this, the number of proper frequencies in any interval $d\nu$ is $4\pi\rho^{3/2}\kappa^{3/2}\nu^2d\nu$ per cm.^{3}

The factor $\rho^{3/2}\kappa_{3/2}$ is $\dfrac{1}{q^3}$, q being the velocity of sound in the space-lattice, which, as shown above, is determined by the atomic volume and the dielectric constant. Now if light be allowed to fall on the metal, it may happen that a sufficiently intense wave is induced in the space-lattice to disrupt it and project an electron. This is the more likely to happen the more proper frequencies there are in the space-lattice in resonance with the incident light-wave. For a given metal this number is proportional to ν^2. The probability of a resonator getting the energy necessary to free an electron $h\nu$ is inversely proportional to ν. Thus the photoelectric current should be proportional to the frequency, which is confirmed by experiments. On the other hand, as shown above, other things being equal, the number of proper frequencies of a given colour is inversely proportional to the third power of the velocity of sound, or roughly to the atomic volume. Thus the theory also accounts for the observed fact that the photoelectric sensibility for red light is greatest with the alkali metals whose atomic volume is greatest. This point of view disposes at once of the

difficulty emphasized by Bragg, that the energy of photo-electrons is often greater than the incident energy of the light falling on one electron. A large part of the wave-front can act upon the electron space-lattice. The additional assumption of zero-point energy would of course still further simplify matters. Whether the selective photo-effect is due to peculiarly numerous proper frequencies within a small region, such as Born and Karman found in ordinary crystals, must be decided by experiment. If, as seems more probable, it is due to other intra-atomic electrons, a gas should show a selective effect though it should not have a normal effect.

Hall Effect.—The Hall effect would be explained exactly as it is done in the ordinary theory. A magnetic field would tend to make the electron space-lattice drift off at right angles as it would do to cathode rays. To explain the inverse Hall effect this theory needs the same hypothesis of atomic magnetic fields as has been introduced to explain the phenomenon on the old lines.

Thomson Effect.—As the electron space-lattice moves, this being the electric current, the temperature inequalities in it may be expected to move with it. The quantitative relations involve, however, the question of the interchange of energy between the atoms and the electrons, and how elementary our knowledge of this question is, is proved by the quantum theory.

Nernst-Ettingshausen Effect.—Though it is probable that a magnetic field must deform a longitudinal elastic wave in an electron space-lattice, thus producing a transverse electro-motive force during heat conduction, the problem cannot be attacked without more detailed knowledge of the interaction of the atoms and electrons.

Hitherto only crystals have been considered, but in the actual metals with which experiments have been made we have to deal with an agglomeration of crystals. Obviously this will not invalidate the conclusions drawn above, for to all intents and purposes all the effects are additive. One could only expect to find a difference if the crystals were of the same order of magnitude as the molecules, for only then would the boundary effects become of the same order as the volume effects. Perhaps the fact that cold drawing increases the resistance of wires, whereas annealing diminishes it, may be an indication that this is true ; for cold drawing obviously breaks up the crystals which tend to join up again through annealing. At first sight one might expect the specific electric resistance of a metal crystal to be different in

different directions. The few measurements available seem to confirm this view, which would not seem to be readily derivable from the old theory. On the other hand, the elastic properties also vary in different axes, and the variation of the atomic amplitudes occasioned thereby might compensate the change in the distance which the electron space-lattice would have to pass through, and thus sometimes mask the phenomenon. This effect would of course not be noticeable in an agglomeration of crystals oriented at random, such as the specimens are which are used for experiments. According to the proposed theory, an increase of pressure would lead to an increase in the atomic frequency and consequently to a decrease in the amplitude. This would entail a decrease in the resistance, such as has been found experimentally. It would seem difficult to explain this phenomenon by the accepted theory. The thermodynamic aspects of the space-lattice theory are particularly simple. As the electrons form a crystal, Nernst's theorem may certainly be applied to them, and all the consequences already deduced by this method hold good. The admissibility of applying this theorem, as has been done, to electrons considered as a perfect gas is much more doubtful *.

It will be objected that the assumption of a force $kf(r)$ and of a number N and a dielectric constant D to satisfy the condition $\phi(N, k) \backsim \psi(N, D)$, are simply made to explain the phenomena, without any regard for *a priori* probability. On the other hand, once these assumptions are made, all the essentially metallic phenomena may be explained without any intrinsic contradictions, including some facts, such as the electrical resistance of alloys and the photoelectric effect, on which the accepted theory throws no light at all.

The accepted theory, besides leading to the absolute contradictions touched upon in the introduction, entails special hypotheses for many of the secondary phenomena. Its one triumph, the derivation of the constant of Wiedemann-Franz's law, is based upon the theorem of the equipartition of energy, whose applicability to electrons as they are supposed to exist, is generally recognized as absolutely inadmissible.

Conclusions.

The free electrons in a metal may not be treated as a gas, for a gas can only conduct heat well if its heat capacity is large. Experiment proves that the free electrons conduct heat well, but that their heat capacity is too small to be

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* E. Grüneisen, *Verh. d. d. Phys. Ges.* xv. 6, p. 186 (1913).

measured.   The assumption of a large free path to compensate a small number leads to contradictions with the optical properties of metals.   It is suggested that the free electrons in a metal form a space-lattice, which corresponds to a crystal at a very low temperature, as the small mass of the electrons leads to a high frequency.   The point of view from which this theory would explain the various metallic phenomena is indicated.   Although it explains the exceptional behaviour of alloys and the general outlines of the photoelectric effect, special assumptions are needed to arrive at the law of Wiedemann-Franz.   The contradictions entailed by the old theory, more especially the one mentioned above, do not arise.

Sidmouth, Dec. 3rd, 1914.

XIII. *The Series Spectrum of Hydrogen and the Structure of the Atom.   By* H. STANLEY ALLEN, *M.A., D.Sc.* [*]

THE series spectrum of hydrogen can be represented with considerable accuracy by the formula of Balmer, which may be written

$$n = N\left(\frac{1}{4} - \frac{1}{m^2}\right), \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where n is the number of wave-lengths per centimetre, N is the series constant, and $m = 3, 4, 5 \ldots$.

In a recent investigation by W. E. Curtis [†] the wave-lengths of the first six lines of the series have been determined with an accuracy of 0·001 Å.U.   It was found that Balmer's formula was inexact.   This was shown by the fact that the values of N calculated by the above expression for the different lines are not the same.   (See Table I., which is reproduced from the paper referred to.)   Curtis found that the results could be better represented by the Rydberg formula,

$$n = \frac{N}{(2+p)^2} - \frac{N}{(m+\mu)^2}. \quad . \quad . \quad . \quad (2)$$

By putting $p = 0$, $\mu = +0 \cdot 0_5 69$, and $N = 109{,}679 \cdot 22$ the formula gives a fit quite within the limits of experimental error.   Very little improvement is obtained by introducing a third constant p.   If this be done the values of the constants are

$$p = +0 \cdot 0_7 8, \quad \mu = +0 \cdot 0_5 70, \quad N = 109{,}679 \cdot 23.$$

In a paper in the Philosophical Magazine on the magnetic field of an atom in relation to theories of spectral series [*], I have shown that a formula of the type given by Ritz can be deduced by the methods of Bohr's theory if the magnetic field of the atom be taken into account. Formula 17 of that paper gives the frequency in the form

$$\nu = \frac{2\pi^2 m e^2 \mathrm{E}^2}{h^3} \left\{ \frac{1}{\left[\sigma_2 + \dfrac{\mathrm{B}}{\sigma_2{}^2}\right]^2} - \frac{1}{\left[\sigma_1 + \dfrac{\mathrm{B}}{\sigma_1{}^2}\right]^2} \right\}, \quad (3)$$

where

$$\mathrm{B} = \frac{16\pi^3 m \mathrm{M} \mathrm{E} e^2}{h^3}. \quad \ldots \ldots (4)$$

Seeing that Bohr's theory of spectral series has achieved its greatest success in dealing with the hydrogen spectrum, it appeared that it would be of special interest to determine whether the inclusion of the effect of a magnetic field would lead to results consistent with observation in this case.

In the case of hydrogen E, the charge on the nucleus, is equal to e, the charge on the electron, and the factor outside the bracket becomes equal to $2\pi^2 m e^4/h^3$, which is equivalent to Rydberg's constant. It has been pointed out by Bohr [†] and Fowler [‡] that a correcting factor must be introduced involving the mass of the electron and that of the core.

In order to test the applicability of the formula to the hydrogen series, we may put $\sigma_2 = 2$, $\sigma_1 = m$ (where $m = 3, 4, \ldots$), B in the first bracket $= 0$ and B in the second bracket $= \dfrac{16\pi^3 m \mathrm{M} e^3}{h^3}$.

It must be noted here that this implies a slight modification of the scheme suggested in the previous paper. For by assigning different values to B in the two brackets we suppose that the magnetic moment of the core (M) has different values in the two types of steady states of motion, the emission taking place in the passage between these types.

The inequality in the order of magnitude of p and μ in the formula of Curtis indicates that the two types of state concerned are in some way different.

The formula for the wave-number may now be written

$$n = \mathrm{N} \left\{ \frac{1}{4} - \frac{1}{\left(m + \dfrac{\mathrm{B}}{m^2}\right)^2} \right\}. \quad \ldots \ldots (5)$$

[*] *Suprà*, p. 40.
[†] Bohr, Phil. Mag. vol. xxvii. p. 509, March 1914.
[‡] Fowler, Bakerian Lecture, Royal Society, 1914.

The applicability of this formula might be tested by finding values of the constants N and B which would yield the closest fit for the wave-numbers observed. It seemed preferable, however, to assume that B could be calculated from formula (4) involving M the magnetic moment of the core on the supposition that this contained an integral number of magnetons. The magnetic moment of the magneton was taken as $1 \cdot 854 \times 10^{-21}$ E.M.U. or $0 \cdot 618 \times 10^{-31}$ E.S.U. It was found that the best results were obtained by taking either 5 magnetons ($B = 5 \cdot 24 \times 10^{-5}$) or 6 magnetons ($B = 6 \cdot 29 \times 10^{-5}$) in the core. The results can be tested by seeing whether constant values are obtained for N when the observed values of n are substituted in formula (5). The values of N calculated on the various assumptions are collected together in Tables I. and II.

TABLE I.
Values of N (Balmer's Law).

Line.	m.	n (observed).	N.	$p.e.$
α	3	15,233·281	109,679·62	± 0·03
β	4	20,564·880	·36	± 0·02
γ	5	23,032·644	·26	± 0·02
δ	6	24,373·165	·24	± 0·03
ϵ	7	25,181·458	·24	± 0·04
ζ	8	25,706·075	·25	± 0·03

TABLE II.
Values of N (suggested Laws).

Line.	m.	Curtis. $\mu = 0 \cdot 0_5 69$.	Allen. M=6 magnetons.	Allen. M=5 magnetons.
α	3	109,679·23	109,679·22	109,679·29
β	4	·23	·29	·30
γ	5	·20	·24	·24
δ	6	·22	·24	·25
ϵ	7	·23	·25	·25
ζ	8	·24	·25	·25
Mean		·225	·25	·26

An examination of the results in Table II. shows that though the values obtained for N by the formula of Curtis are slightly more consistent among themselves than those obtained on the hypothesis of magnetic action, the divergence in the latter case is not too large to make this hypothesis untenable. The results with 5 magnetons are slightly better than those with 6 magnetons.

In support of the view that the core contains 5 magnetons we have the fact, first pointed out by Chalmers, that the magnetic moment produced by an electron moving in a circular orbit with angular momentum $h/2\pi$ is exactly 5 magnetons.

The value of the series constant N would then be 109,679·26, and the convergence frequency of the series would be 27419·815. These values differ but little from those given by Curtis, and consequently the wave-lengths of the remaining lines of the series would be practically identical with those given in Table V. of his paper.

On the other hand, the hypothesis that the core contains 6 magnetons appears to receive support from the observed diamagnetic properties of hydrogen, and it may be pointed out that the magnetic moment of the core in this type of state would then be 3 times (corresponding to $m=3$) the moment of a sphere rotating with the angular velocity specified in earlier papers. This would give 109,679·25 as the series constant, and 27419·813 as the convergence frequency.

Thus it appears that it is possible to account for the series spectrum of hydrogen on the lines of Behr's theory combined with the assumption that the core of the atom can produce a magnetic field equivalent to that set up by either 5 or 6 magnetons.

In conclusion, I desire to express my thanks to Professors J. W. Nicholson and O. W. Richardson for their advice and suggestions.

University of London, King's College.

XIV. *On the Variation of the Triple-Point of a Substance with Hydrostatic Pressure.* By ALFRED W. PORTER, *D.Sc., F.R.S.*[*]

THE fact, the truth of which is now well recognized, that the saturation vapour-pressure of any liquid or solid is a function of the hydrostatic pressure, carries with it sundry consequences. One of these is that the triple-point

must no longer be considered as a fixed point but as a point which also varies with change in the hydrostatic pressure. That this must be the case can be seen almost immediately. Recall that the triple-point is the temperature at which the vapour-pressure curves of the solid and liquid meet ; so that, if this temperature is exceeded, we can only have liquid and its vapour in equilibrium together ; and if it is not reached we can only have solid and its vapour.   Now the position of the triple-point for ice-water-steam, as usually determined, is at ·0074° C.   Let the hydrostatic pressure, however, be raised (for example) to one atmosphere : the melting-point of ice becomes 0° C.   If the triple-point is a fixed point we shall, under these conditions, have a range of temperature from 0° C. to ·0074° C. for any point of which it may be said that hoar-frost cannot form because the substance is above the freezing-point, and dew cannot form because it is below the triple-point.   It is clear that this dilemma can be resolved only by postulating that the triple-point must have moved to the freezing-point, viz. 0^c C., corresponding to the hydrostatic pressure of one atmosphere.

   This can be proved by a more detailed examination in which proper account is taken of the variation of vapour-pressure with hydrostatic pressure.   We will first of all prove an auxiliary theorem.

<div align="center">

The slopes of the vapour-pressure curves
near the triple-point.

</div>

   In determining these slopes it is customary to take Clapeyron's equation

$$L_{12} = T(v_2 - v_1)\frac{d\pi}{dt}$$

for the three possible variations, and by neglecting $v_1 v_2$, the volumes of ice and water, in comparison with that of the vapour, v_3, to obtain the approximate equations :

$$L_{13} = Tv_3 \frac{d\pi_{13}}{dt},$$

$$L_{23} = Tv_3 \frac{d\pi_{23}}{dt},$$

$$L_{12} = T(v_2 - v_1)\frac{d\rho_{12}}{dt};$$

whence, since at the triple-point

$$L_{13} = L_{12} + L_{23}$$

we obtain

$$\frac{d\pi_{13}}{dt} - \frac{d\pi_{23}}{dt} = \frac{v_2 - v_1}{v_3}\frac{dp_{12}}{dt}.$$

This gives an approximate value for the difference of slopes of the two vapour-pressure curves.

We will now show by a more precise treatment, in which proper allowance is made for the variation of vapour-pressure with hydrostatic pressure, that this equation is not approximate merely, but exact when certain exact meanings are given to $\frac{d\pi_{13}}{dt}$ and $\frac{d\pi_{23}}{dt}$.

The hydrostatic pressure may be imagined to be applied by means of a permanent gas placed in the vapour chamber. It is much better, however, if we make use instead of a semi-permeable membrane which separates the liquid and vapour

Fig. 1.
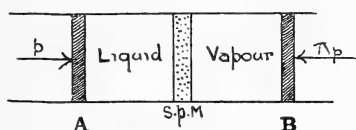
one from the other ; so that, if the membrane is permeable to the vapour alone, any pressure whatever, p, may be imposed on the liquid, and the vapour will then be able to take up the vapour-pressure π_p which corresponds to this hydrostatic pressure. With such an arrangement, shown more in detail in fig. 1, a cycle of operations can be made, each reversible in character, and the mechanical efficiency of this cycle may be given its universal value $\frac{dT}{T}$.

In estimating the work done during the cycle we note that this is given directly as the sum of all such values as $\int pdv$ for its various stages. Great simplification is brought about, however, if use be made of the facts that

$$\int_1^2 pdv = p_2 v_2 - p_1 v_1 - \int_1^2 vdp \text{ always ;}$$

and that for any cycle of operations the sum of all the values of $p_2 v_2 - p_1 v_1$ is necessarily zero, and therefore the work done is given by the sum of all the values of $-\int vdp$.

Imagine then a four-stage cycle performed, and estimate

the value of this latter quantity for each stage. We will call the separate values S_1, S_2, S_3, S_4.

i. Move the pistons A and B from left to right so that one gram of liquid evaporates at constant pressure.

$S_1 = 0$ because the pressures p and π_p keep constant.

ii. Raise the temperature an amount dT. This change increases the pressure of liquid and vapour by $\dfrac{\partial p}{\partial T} dT$ and $\dfrac{\partial \pi_p}{\partial t} dT$ respectively.

[*Note.* Part of the change in π_p will be consequent on the change in temperature (p constant) and part on the change of p itself.]

If U and V were the initial volumes of the liquid and vapour, and u_p and v_π their specific volumes, the volumes during stage ii. are $U - u_p$ and $V + v_\pi$ respectively.

We have therefore

$$S_2 = (U_p - u_p) \frac{\partial p}{\partial T} dT + (V + v) \frac{\partial \pi_p}{\partial T} dT.$$

iii. Push the vapour back into the liquid at the constant temperature $T + dT$ and the constant pressures $\pi_p + \dfrac{\partial \pi_p}{\partial T} dT$ and $p + \dfrac{\partial p}{\partial T} dT$ respectively.

$S_3 = 0$ because the pressures keep constant.

iv. Lower the temperature by the amount dT.

$$S_4 = - U \frac{\partial p}{\partial T} dT - V \frac{\partial \pi_p}{\partial T} dT.$$

Now the heat given out at the higher temperature is L, the latent heat of vaporization. Hence

$$\frac{\Sigma (p dv)}{-L} = \frac{dT}{T}$$

or

$$\left(v_\pi \frac{\partial \pi_p}{\partial T} - u_p \frac{\partial p_p}{\partial T} \right) T = L.$$

The cycle here employed can of course be exhibited graphically. It is best to employ two diagrams—one for the liquid and the other for the vapour.

The cycles for the two will be traversed opposite ways because when the total volume of the liquid diminishes

Fig. 2.
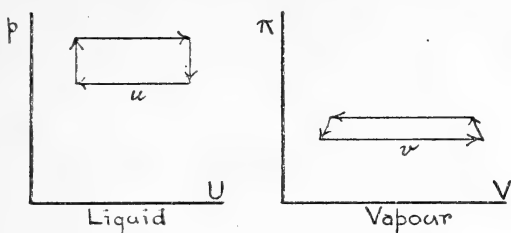
that of the vapour increases. The final equation can be obtained almost by inspection. The sense in which the cycles have been traversed happens to be that in which the heat taken in at the higher temperature is $-L$. They could equally well be taken with their directions both reversed, the sign of the heat entry being reversed simultaneously. The ordinary equation is obtained from this by taking p as the pressure of the vapour alone, for it corresponds to the case in which the liquid and vapour are in contact without any intervening semi-permeable membrane. Both are then at the same pressure, at any rate when capillary and other special surface forces are absent.

For this ordinary case $\dfrac{\partial p}{\partial T}$ also equals $\dfrac{\partial \pi}{\partial T}$, and consequently

$$L = T(v - u)\frac{\partial \pi}{\partial T}.$$

This equation is of course exact *for the special circumstances to which it relates;* it is not the general equation, however.

Another special case is that in which the pressure p of the liquid is kept constant throughout the cycle. This can be done; for the variations of p can be made independently of T. In this special case we obtain

$$L = Tv\left(\frac{\partial \pi}{\partial T}\right)_p.$$

The meaning of L in all these expressions is absolutely the same; but it is expressed in slightly different terms.

Let now a diagram be made in which it is these values of π, corresponding to different temperatures but to precisely the same hydrostatic pressure, which are plotted against the temperature. There will be two such curves, one for the

solid and one for the liquid.   The difference of the slopes of these curves at their point of intersection will be given *exactly* by the equation

$$\frac{\partial \pi_{13}}{\partial T} - \frac{\partial \pi_{23}}{\partial T} = \frac{u_2 - u_1}{v} \frac{dp_{12}}{dT},$$

where the specific volumes of the liquid and solid are represented by u_2 and u_1.   Fig. 3 is such a diagram.

The locus of the triple-point.

On this diagram the vapour-pressures are shown for two hydrostatic pressures differing by dp.   Their point of intersection shifts from C to C' owing to this change of pressure,

Fig. 3.
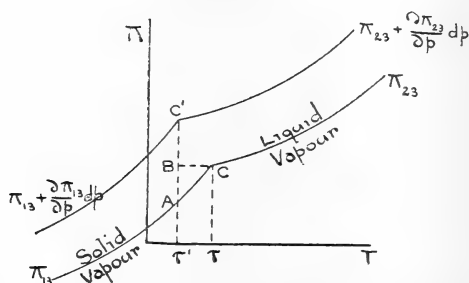
and the temperature of the triple-point shifts from τ to τ' or through the amount $\frac{d\tau}{dp} dp$.   Draw a vertical through C' cutting the lower curve at A, and draw a horizontal through C cutting this vertical at B.   Then

$$AC' = AB + BC'$$

or

$$\left(\frac{\partial \pi_{13}}{\partial p}\right)_T dp = -\frac{\partial \tau}{\partial p} dp \left\{ \left(\frac{\partial \pi_{13}}{\partial T}\right)_p - \left(\frac{\partial \pi_{23}}{\partial T}\right)_p \right\} + \left(\frac{\partial \pi_{23}}{\partial p}\right)_T dp \; *,$$

as can be seen by inspection of the figure.

* This can be obtained at once from the general expression for the total differential of the vapour-pressure in passing from one triple-point to another :

$$d\pi = \frac{\partial \pi_{23}}{\partial p} dp + \frac{\partial \pi_{23}}{\partial T} d\tau$$

$$= \frac{\partial \pi_{13}}{\partial p} dp + \frac{\partial \pi_{13}}{\partial T} d\tau.$$

Now make use of the relation for the slopes of the curves, and we get

$$\left(\frac{\partial \pi_{13}}{\partial p}\right)_{\mathrm{T}} dp - \left(\frac{\partial \pi_{23}}{\partial p}\right)_{\mathrm{T}} dp = -\frac{\partial \tau}{\partial p} dp \frac{u_2 - u_1}{v} \frac{dp_{12}}{d\mathrm{T}}.$$

But $\left(\dfrac{\partial \pi_{13}}{\partial p}\right)_{\mathrm{T}}$ is the variation coefficient of π_{13} with regard to p at constant temperature ; and this is known to be $\dfrac{u_1}{v}$; similarly

$$\left(\frac{\partial \pi_{23}}{\partial p}\right)_{\mathrm{T}} = \frac{u_2}{v} ;$$

so we obtain finally

$$\frac{d\tau}{dp} = \frac{d\mathrm{T}}{dp_{12}} ;$$

that is, the variation of τ, the temperature of the triple-point, with hydrostatic presure is equal to the variation of the melting-point with hydrostatic pressure.

It should be observed that $\dfrac{d\tau}{dp}$ is not the slope of the line CC' on the π, T diagram, but the slope of the corresponding curve on a p, τ diagram.

This question has been here discussed with special reference to the case of ice-water-steam. But the results obtained are of course general for all triple-points and can be extended to the case of multiple-points.

Dec. 5th, 1914.

XV. *On the Form of a Liquid Drop suspended in another Liquid, whose density is variable.* By JAMES RICE, *M.A.*, *Lecturer in Physics, Liverpool University* [*].

IN the August number of the Phil. Mag., Lord Rayleigh has considered the Equilibrium of Revolving Liquid under Capillary Force.

The following paper offers a partial solution to a similar problem, viz., to discover the form assumed by a liquid drop suspended in another liquid, whose density varies with the depth.

The investigation was suggested by an effect which is observed in carrying out the well-known experiment of

Plateau, in which a drop of oil is suspended in a mixture of water and alcohol having the same density as the oil. If it happens that the evaporation of the alcohol from the surface of the mixture produces a density-gradient in the latter, then the drop of oil flattens into an oval form.

It is assumed that the density of the surrounding liquid varies continuously with the depth.
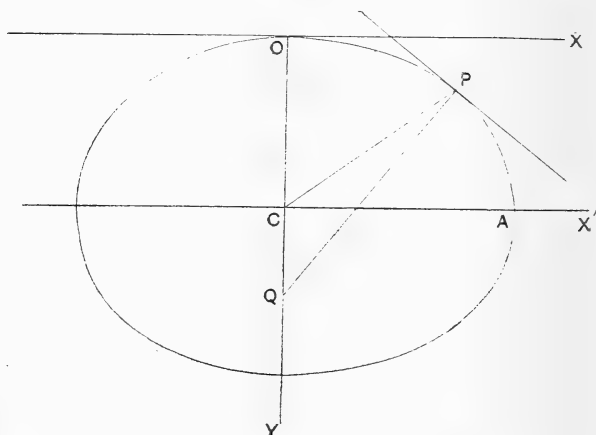
The figure represents a vertical section of the drop (which is of course a surface of revolution) through its highest point. The axes are in the first instance tangent and normal to the section at this point.

Let σ represent the constant density of material of the drop, and ρ the variable density of the surrounding liquid.

Then $$\rho = \rho_1 f(y)$$

where ρ_1 is the liquid-density at the level of O, and $f(y)$ is a function of y which approaches the value unity as y approaches zero.

Let R be the radius of curvature at P, and R_1 that at O. One easily obtains as the condition of equilibrium

$$T\left(\frac{1}{R} + \frac{1}{PQ}\right) = \frac{2T_1}{R_1} + g\sigma y - g\int_0^y \rho\, dy,$$

where T represents surface-tension. If we assume this to be uniform, it is easily shown that the places of maximum surface-curvature lie in the level at which the densities of the drop and the surrounding liquid are equal.

For at such a point

$$\frac{d}{dy}\left(\frac{1}{R} + \frac{1}{PQ}\right) = 0,$$

and therefore if T is constant

$$\frac{d}{dy}\left(\sigma y - \int_0^y \rho\,dy\right) = 0,$$

i.e.,
$$\sigma = \rho.$$

Without analysis this is evident from the following consideration. A difference of pressure exists between points at the same level, inside and outside the drop, and this difference is proportional to the curvature of the drop at this level. Such difference of pressure increases from the top of the drop until the level of equal densities is reached, since in this region the density of the drop exceeds that of the surrounding liquid. Thereafter, the pressure-difference decreases ; for below the level of equal densities the density of the drop is the lesser.

Let us assume as a further restriction that

$$\rho = \rho_1\left(1 + \frac{v}{h}\right)$$

where h is a linear constant.

We readily obtain

$$\frac{1}{R} + \frac{1}{PQ} = \frac{2}{R_1} + \frac{g(\sigma - \rho_1)}{T}\cdot y - \frac{1}{2}\frac{g\rho_1}{T}\cdot\frac{y^2}{h},$$

or putting
$$b = \frac{\sigma - \rho_1}{\rho_1}\cdot h$$

and
$$c^2 = \frac{T}{g\rho_1},$$

$$\frac{1}{R} + \frac{1}{PQ} = \frac{2}{R_1} + \frac{y(2b - y)}{2hc^2}.$$

It is easily seen that $y = b$ is the level of equal densities and maximum curvature. In other words, $2b$ is the vertical height of the drop.

Transfer the axis of x to CAX′ at this level, and the above equation becomes

$$\frac{1}{R} + \frac{1}{PQ} = \frac{2}{R_1} + \frac{b^2 - y^2}{2h\cdot c^2}. \quad \cdots \quad (1)$$

This equation shows that the curvatures at points equidistant from the level CX', above or below, are equal. The symmetry with respect to this level is an obvious consequence of the assumed uniformity of the density gradient.

It is not difficult to show that an ellipse of small eccentricity is a possible form of meridianal section.

For this to be so it is necessary according to the previous equation that

$$\frac{ab}{b'^3} + \frac{b}{ab'} = \frac{2b}{a^2} + \frac{b^2 - y^2}{2hc^2},$$

where $\qquad a = \text{CA},$

$\qquad\qquad\qquad b = \text{CO},$

and $\qquad\qquad b' = $ the semidiameter conjugate to CP.

If ϕ is the eccentric angle of **P**, this reduces to

$$\frac{b}{a^2} \left\{ \frac{1}{(1 - e^2 \cos^2 \phi)^{\frac{3}{2}}} + \frac{1}{(1 - e^2 \cos^2 \phi)^{\frac{1}{2}}} - 2 \right\} = \frac{b^2}{2hc^2} \cos^2 \phi,$$

i. e., to

$$\left(\frac{3}{2} + \frac{1}{2} \right) e^2 \cos^2 \phi + \left(\frac{15}{8} + \frac{3}{8} \right) e^4 \cos^4 \phi + \&c.,$$

$$= \frac{a^2 b}{2hc^2} \cos^2 \phi.$$

If $\qquad\qquad e^2 = \dfrac{a^2 b}{4hc^2} = \dfrac{3 \times \text{volume of drop}}{16\pi hc^2},$

and if also e were so small that e^4, e^6, &c. could be neglected in comparison with e^2, the above equation would be approximately satisfied.

It is clear that for a similar order of approximation, a larger drop is possible, the greater the values of h and c.

The method employed by Lord Rayleigh, in which the differentials of the coordinates with respect to the arc are used, does not, unfortunately, lead to an equation so readily integrable as the one preceding equation (3) of his paper. Still some headway may be made, although the approximations, if pushed very far, would become excessively laborious.

E. g., the equation (1) becomes in these terms,

$$\frac{\dfrac{d}{ds} \left(x \dfrac{dy}{ds} \right)}{x \dfrac{dx}{ds}} = \frac{2}{\text{R}_1} + \frac{b^2 - y^2}{2hc^2} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

The difficulty of solution arises from the fact that the right hand expression in (2) is a function of y and not of x (as is the case in Lord Rayleigh's paper).

However, remembering that the curve is symmetrical with regard to the axes, we may write

$$b^2 - y^2 = \alpha x^2 + \frac{x^4}{l^2} + \ldots,$$

where α and l are to be found by approximation from (2).

E. g., the approximately elliptical form discovered above can be found by using as the first approximation

$$b^2 - y^2 = \alpha x^2,$$

where α ($= 1 - e^2$) is a ratio slightly less than unity.

After substitution and an integration, (2) then leads to

$$\frac{dy}{ds} = \frac{x}{R_1} + \frac{\alpha x^3}{8hc^2},$$

no constant being required.

Also
$$\frac{dx}{ds} = -\frac{y}{\alpha x}\frac{dy}{ds},$$

and, therefore, since

$$\left(\frac{dx}{ds}\right)^2 + \left(\frac{dy}{ds}\right)^2 = 1,$$

we obtain

$$\left(\frac{1}{R_1} + \frac{\alpha x^2}{8hc^2}\right)^2 \left(x^2 + \frac{b^2 - \alpha x^2}{\alpha^2}\right) = 1. \quad \ldots \quad (3)$$

On expanding and equating the constant term to unity, and the coefficient of x^2 to zero, we find that α is given by

$$\alpha(1 - \alpha) = \frac{b^3}{4hc^2},$$

or
$$e^2 = \frac{b^3}{(1 - e^2)4hc^2} = \frac{a^2 b}{4hc^2},$$

as before.

It will also appear that with a sufficiently small value of e^2 or $1 - \alpha$, that the terms on the left of (3) which involve x^4 and x^6 are negligible.

E. g., the term in x^4 turns out to be

$$\frac{3}{64} \cdot \frac{b^2}{h^2 c^4} \cdot x^4.$$

Its maximum value is

$$3a^4 b^2 / 64 h^2 c^4 \quad \text{or} \quad \frac{3}{4} \cdot e^4.$$

By applying the same method to the approximation containing a fourth power of x, I find that an approximate solution is given by

$$b^2 - y^2 = \alpha x^2 + \frac{(1-\alpha)^2 x^4}{4b^2},$$

where α is chosen to have a value slightly less than **unity**, and b is then determined by

$$b^3/4hc^2 = \alpha(1-\alpha) + (1-\alpha)^2/\alpha.$$

The steps are laborious, and it is not necessary to reproduce them. The solution is the oval of a quartic curve (which also possesses imaginary parabolic branches). It is clearly slightly less eccentric than the approximate elliptic solution. It is nearer the truth, inasmuch as the steps leading to it involve the neglect of terms in $(1-\alpha)^3$ and higher powers, whereas the elliptic solution neglected terms in $(1-\alpha)^2$.

XVI. *On the Spectrum of Palladium.*
By Dr. Emil Paulson [*].

KAYSER [†] was the first to show the existence of triplets in the spectrum of Palladium. This was found by him to be repeated 6 times completely and 3 times incompletely in the whole spectrum. Designating the wave-number of the first line in each triplet by A and those of the two other lines by B and C respectively, the wave-numbers of the triplet are given by the relations :

$$B = A + 3967 \cdot 90 \qquad \Delta_1 = 3967 \cdot 90$$
$$C = A + 5159 \cdot 09 \qquad \Delta_2 = 1191 \cdot 19,$$

Δ_1 and Δ_2 being the differences of the components of the triplets.

Afterwards, without being aware of the work of **Kayser**, I [‡] discovered the pairs with the difference 1191, but did not find the complete triplet ; I also found many other pairs with the differences 1628 and 403 respectively. It was, however, to be assumed that all these pairs and triplets could be

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[*] Communicated by the Author.

[†] H. Kayser, " Die Spectren der Elemente der Platingruppe," *Abh. d. Berl. Akad.* 1897 ; Astrophys. J. vii. 1899.

[‡] E. Paulson, " Beiträge zur Kenntnis der Linienspectren," Diss. Lund, 1914, pp. 33–34.

brought together in greater groups of lines in conformity with what I have found in several other spectra *.

In fact a line has been omitted by Kayser, so that his difference 3968 is the sum of two differences with the values 1628 and 2340. The first of these I have already given in my thesis above referred to. Thus, the complete group contains 4 lines. It seems, however, as if one line more should be included. This appears only three times, but it follows from its intensity and general appearance, that it belongs to the same group.

In the table below are given certain wave-numbers † of lines in the Pd-spectrum, which are arranged in such a way that lines belonging to two corresponding columns A–D in all the rows (1–21) show the same differences. These differences are given in the columns headed Δ_1, Δ_2, and Δ_3. In the last of these columns, Δ_3, the difference 7757 has also been inserted in brackets. The wave-numbers of the corresponding lines (E) are placed in column D. Lastly, the mean of each difference is given at the foot of the table.

The wave-numbers of the lines in succeeding columns in the table above are given by the relations :

$$B = A + 1628 \cdot 33$$
$$C = A + 3968 \cdot 00$$
$$D = A + 5159 \cdot 14$$
$$(E = A + 11725 \cdot 45).$$

It will be noticed that, excepting the lines 3404 (10R), 3380 (5u), 3142 (6), 2763 (8R), and 2441 (6R), all strong lines for the interval 4213 to the end of the spectrum are embodied in the above mentioned system. Among the lines with larger wave-lengths it gives, indeed, many with stronger intensities which cannot be placed in the system.

We will next consider how these lines, without doubt standing in a certain connexion to one another, are divided in the electromagnetic field. The separation of the lines is indeed very different in the same group as well as by passing from one group to another and does not indicate any simple relation between the lines, for instance that the groups should be produced by the same electron.

---

* " On the Spectrum of Yttrium," being printed in the Astrophys. J. ; " Ein System von Wellenzahlen im Scandiumspektrum," *Phys. Zeitschr.* 1914, p. 892; " Gesetzmässigkeiten im Bau des Lanthanspektrums," *Ann. d. Physik*, xlv. p. 1203 (1914).

† The measurements of the wave-lengths are taken from Kayser.

	I.	A.	Δ₁.	I.	B.	Δ₂.	I.	C.	Δ₃(and Δ₁)	I.	D (and E).
1	...	...	...	0	18702·15	...	6	19565·88	1191·08	9	20756·96
2	...	19552·14	...	5	...	...	...	...	3530·89	2	22233·04
3	2	22352·51	1628·15	10	23980·76	3968·14	1	22520·28	1191·10	...	...
4	7	23735·88	1628·26	4R	...	2339·67	5R	22632·43	1191·16	10R	27511·53
5	6R	24464·71	1628·21	7R	26092·97	3967·75	9R	27703·13	[7757·33]	7R	28894·29
6	6	25260·31	1628·15	0	20888·52	2339·62	8R	28432·59	1191·30	8R	36189·92
7	5R	25678·30	...	...	...	2339·54	8R	29228·06	1191·39	5	30419·36
8	6R	27096·67	...	...	28724·82	3967·67	6R	29645·97	...	10R	30837·36
9	6R	...	...	...	29445·71	2339·87	4	31064·69	1191·08	...	...
10	...	...	...	...	...	2339·88	1	31785·59	[7757·56]	4R	33302·47
11	7R	28143·33	1628·51	6R	30282·38	3968·06	5R	32111·39	1191·16	10R	40379·41
12	4R	28653·87	1628·43	6R	30685·11	2339·47	4R	32621·85	[7757·37]	7R	34215·88
13	9R	29066·68	1628·54	5R	30752·66	2339·66	4R	33024·77	1190·93	10R	40849·67
14	5R	29124·12	...	...	...	2339·64	3	33092·30	1191·13	2	36462·68
15	...	...	...	...	...	...	0	35271·75	...	1	38801·80
16	...	34030·39	...	...	...	...	2	37610·67	...	...	...
17	0	...	...	0	...	3968·01	0	37998·40	1190·73*	2	41098·14
18	...	37368·51	...	...	...	...	2	39907·41	5158·80	0	42527·31
19	2	...	...	...	39243·85	...	...	...	3530·68	1	42774·53
20	...	39198·78	...	...	...	3968·49	...	4167·27	1190·43*	1	44357·70
21	0	...					0				
		Mean	1628·33		Mean	2339·67		Mean	1191·14		
						3968·00			3530·81		
									5159·14		

* Not included in the mean.

Certain regularities exist, however, and ought not to be passed without mention. The lines in the groups 5 and 13 are divided in the following way [*] :

$$
\text{Group 5} \begin{cases} \text{A (6R) Tripl.} & +1\cdot54 & 0 & -1\cdot53 \\ \text{B} - \\ \text{C (9R) Tripl.} & +1\cdot54 & 0 & -1\cdot55 \\ \text{D (7R) Quadr.} & +2\cdot19 & +1\cdot05 & -1\cdot05 & -2\cdot19 \end{cases}
$$

$$
\text{Group 13} \begin{cases} \text{A (9R) Tripl.} & +1\cdot50 & 0 & -1\cdot53 \\ \text{B (6R) Quadr.} & +2\cdot24 & +0\cdot84 & -0\cdot84 & -2\cdot25 \\ \text{C (4R) Tripl.} & +1\cdot53 & 0 & -1\cdot54 \\ \text{D (7R) Sep. unknown.} \end{cases}
$$

The first and the third lines in both these groups become triplets with identical values of $\dfrac{d\lambda}{\lambda^2}$ for all the lines. The second and fourth lines are divided into four constituents each. If also here the values of $\dfrac{d\lambda}{\lambda^2}$ are the same, cannot be determined.

The lines in the groups 12 and 14 are divided in the following manner :—

$$
\text{Group 12} \begin{cases} \text{A (4R) Tripl.} & +1\cdot64 & 0 & -1\cdot63 \\ \text{B (6R) Doubl.} & +0\cdot72 & & -0\cdot72 \\ \text{C (4R) Sep. unknown.} \\ \text{E (10R)} & \text{,,} \end{cases}
$$

$$
\text{Group 14} \begin{cases} \text{A (5R) Tripl.} & +1\cdot68 & 0 & -1\cdot71 \\ \text{B (5R) Doubl.} & +0\cdot65 & & -0\cdot65 \\ \text{C (3) Sep. unknown.} \\ \text{E (10R)} & \text{,,} \end{cases}
$$

The separation is only known for the first two lines, which became triplets or doublets, with probably identical values of $\dfrac{d\lambda}{\lambda^2}$. Both groups contain the line E instead of D.

In group 8 all the lines are divided into triplets. The values of $\dfrac{d\lambda}{\lambda^2}$ are probably the same :—

$$
\text{Group 8} \begin{cases} \text{A (6R) Tripl.} & +2\cdot10 & 0 & -2\cdot12 \\ \text{B} - \\ \text{C (6R) ,,} & +1\cdot98 & 0 & -2\cdot00 \\ \text{D (10R) ,,} & +1\cdot90 & 0 & -1\cdot89 \end{cases}
$$

For the other groups there are not sufficient measurements for comparison, although some other similarities could be pointed out.

Lund, Oct. 1914.

[*] After J. E. Purvis, Proc. of the Cambr. Phil. Soc. vol. xiii. (1906) p. 326.

XVII. *On Lorentz's Theory of Long Wave Radiation.*
By G. H. LIVENS [*].

THE Lorentz form of the theory of radiation, which regards the radiation from a thin metallic plate as arising from the motion of the electrons inside the plate, will probably always remain as a deciding factor in the general theory of this subject, since it involves no principles which cannot certainly be regarded as well established by independent theory and experiment. The final formula to which this theory leads and the extent to which it depends on the assumptions made must therefore be matters of the first importance in the general theory. Basing mainly on the two assumptions that the period of the radiation considered is long compared with the interval of time between two consecutive collisions of an electron with an atom and that this latter interval is also long compared with the time of duration of a collision, Lorentz derives a formula, identical with the Rayleigh-Jeans formula, which is apparently correct in the long wave part of the spectrum but fails hopelessly for obvious reasons in the visible and ultraviolet regions. These two assumptions of course naturally restrict the analysis to long waves, but it is the expressed opinion of Prof. Lorentz [†] that the same Rayleigh-Jeans formula would be obtained as the general result for the other parts of the spectrum if only the difficulties of the analysis could be overcome. The main object of the present paper is the discussion of a partial generalization of Lorentz's analysis, in which one of the two above-mentioned restrictions is removed. A formula, which is concluded to be practically identical with the Rayleigh-Jeans formula, and applicable to all parts of the spectrum, is obtained on the single assumption that the duration of the impact of an electron with an atom is always negligibly small ; and the conclusion carries with it a partial confirmation and possible limitation of a certain well-known result in the optical theory of metals.

The method to be followed is identical with that given by Lorentz with the single exception that it will not be found necessary to assume the relation between the period of oscillation and time interval between successive collisions which is implied in his theory. It is, however, necessary to retain the assumption he makes regarding the smallness of duration of a collision in order to avoid making arbitrary

[*] Communicated by the Author.
[†] See "Discussion on Radiation," B.A. Report, 1912.

hypotheses regarding the dynamical character of the collisions. The case to be analysed is, therefore, virtually that in which the electrons and molecules are assumed to be perfectly rigid elastic spheres, the molecules being, however, of comparatively large mass so that their energy and motion may be neglected.

I do not find it necessary to depart very widely from Lorentz's admirable exposition of his theory given in his book 'The Theory of Electrons'[*], and I shall take the liberty of quoting verbally in many cases from his work, to which I must here acknowledge my great indebtedness.

We will, therefore, with Lorentz, consider a thin metallic plate in which a large number of free electrons are moving about in a perfectly irregular manner, consistent with the general laws of the conservation of their total energy and momentum. We know that an electron can be the centre of an emission of energy when its velocity is changing, thus, as a result principally of the numerous collisions of the electrons with the atoms, resulting in alterations of the directions and magnitudes of the velocities of the electrons, a part of the heat energy of the irregular motion of the electrons will be radiated away from the metal. This radiant energy, which is subsequently to be the subject of a detailed examination, is, however, presumed to be so small compared with the energy of motion of the electrons that it can be neglected in any dynamical considerations respecting those motions extended over any finite time. To this extent the analysis offered is only a first order approximation to the actual state of affairs.

We know also, that as a result of the same collisions between the electrons and atoms, part at least of any regular or organized energy acquired by the electrons during their free motion between the atoms can be dissipated into heat energy of the irregular motion of the same electrons. In this way it is possible for a metal to absorb a portion of the energy from an incident beam of radiation, because the electric force in the electromagnetic field associated with the radiation will pull the electrons about during their otherwise free motion between collisions, imparting kinetic energy to them which will be dissipated by collision at the end of each path into irregular heat-motion.

Now let w and w' be two infinitely small parallel surface elements, w being on the plate itself and w' at a distance r outside it on the normal to the plate through the centre of w. Then of the whole radiation emitted by the metal

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[*] The Theory of Electrons (Leipzig, 1909), Chapter II.

plate, a certain portion will travel outwards through w and w'. Suppose we decompose this radiation into rays of different wave-lengths and each ray again into its plane-polarized constituents in two planes at right angles through the chosen normal to the plate (these two planes and the plane of the plate being parallel to a system of properly chosen rectangular coordinate planes in which $z=0$ is the plane of the plate). Now consider in particular those of the rays in this beam whose wave-length lies between the two infinitely near limits λ and $\lambda+d\lambda$ and which are polarized in the plane $y=0$; the amount of energy emitted by the plate per unit time through both elements w and w' so far as it belongs to these rays, must be directly proportional to w, w', and $d\lambda$ and inversely proportional to r^2, and it can therefore be represented by an expression of the form

$$\mathrm{E}\,\frac{ww'd\lambda}{r^2}.$$

The coefficient E is called the *emissivity* of the plate and is a function not only of the positions of w, w', and λ but also of the conditions and type of the metal composing the plate.

Let us now consider the opposite process. Suppose that a plane-polarized beam such as that specified in the previous paragraph is incident, through the small surface w', on the patch w of the metal plate : then we know that a certain portion of the energy of this beam will be absorbed in the metal and converted into heat-energy, instead of being re-emitted as a portion of the reflected or transmitted beams. The fraction expressing the proportion of the energy absorbed is called the *coefficient of absorption* of the plate under the conditions specified, and is denoted by A.

Starting from the thermodynamic principle that in a system of bodies having all the same temperature, the equilibrium is not disturbed by their mutual radiation, Kirchhoff finds that the ratio

$$\frac{\mathrm{E}}{\mathrm{A}} = \frac{c}{8\pi}\mathrm{F}(\lambda, \mathrm{T})$$

between the emissivity and absorbing powers under the same conditions is independent both of the direction of polarization and the position and peculiar properties of the metal plate. This ratio, a function merely of the temperature T and wave-length λ, is now the chief object of search in the general theory of radiation, determining as it does the complete circumstances of the steady thermal radiation from any body.

But in the conceptions we have adopted, the calculation of both E and A under the assumptions specified can be directly accomplished.

If we consider that the thickness Δ of the metallic plate is so small that the absorption may be considered as proportional to it, we shall find by an obvious calculation, after Lorentz, that

$$A = \frac{\sigma}{c}\Delta *,$$

c being the usual velocity constant and σ the conductivity of the metal.

Now the interpretation of σ in terms of the electron constants of the metal, although a matter of some difficulty, is nevertheless fairly certain †. If N denote the number of free electrons per unit volume in the metal, each of mass m and with a charge e, moving with velocities the average square of which is u_m^2, then we know that in all applications involving steady or slowly varying currents the conductivity σ_0 is given by

$$\sigma_0 = \sqrt{\frac{8}{3\pi}}\,\frac{Ne^2l_m}{mu_m},$$

wherein l_m is a constant, a certain mean length of path, which is determined by the formula

$$l_m = \frac{1}{n\pi R^2},$$

in which n is the number of atoms per unit volume in the metal and R the sum of the radii of an atom and an electron.

However, in applications involving more rapid alternations in the current the above formula is found to be insufficient and requires modification along lines already laid down by various authors. According to Jeans ‡ the correct form to be used for alternating currents with a frequency $\frac{c}{\lambda}$ is

$$\sigma = \frac{\sigma_0}{1 + \dfrac{4\sigma_0^2\pi^2c^2m^2}{\lambda^2N^2e^4}},$$

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* 'The Theory of Electrons,' p. 280 (note 33).
† 'The Theory of Electrons,' chapter I., and p. 266 (note 29).
‡ Phil. Mag. June 1909.

or, on substitution of the value of σ_0, we get

$$\sigma = \sqrt{\frac{8}{3\pi}} \ \frac{\dfrac{Ne^2 l_m}{mu_m}}{1 + \dfrac{32\pi c^2 l_m{}^2}{3\lambda^2 u_m{}^2}} \ .$$

a formula reducing to the Lorentz-Drude formula for large values of λ.

We have therefore for the coefficient of absorption under the conditions specified and for plane-polarized radiation of wave-length λ,

$$A = \sqrt{\frac{8}{3\pi}} \ \frac{\dfrac{Ne^2 l_m \Delta}{mu_m}}{1 + \dfrac{32\pi c^2 l_m{}^2}{3\lambda^2 u_m{}^2}} \ .$$

Now let us consider the radiation from the plate, still closely and often verbally following Lorentz. We need only consider the radiation normally from the small volume $w\Delta$ of the plate, as this is the only part of all the radiation through w from the whole plate that gets through w'. Now according to a well-known formula of electrodynamics, a single electron moving with a velocity v (a vector with components v_x, v_y, v_z) in the part of the plate under consideration, will produce at the position of w' an electromagnetic field in which the x-component of the electric force is given by

$$- \frac{e}{4\pi c^2 r} \ \frac{dv_x}{dt},$$

if we take the value of the differential coefficient at the proper instant. But on account of the assumption as to the thickness of the plate, this instant may be represented for all the electrons in the portion $w\Delta$ by $t - \dfrac{r}{c}$, if t is the time for which we wish to determine the state of things at the distant surface w'. We may therefore write for the x-component of the electric force in the total field at w'

$$E_x = - \frac{1}{4\pi c^2 r} \left[\sum e \frac{dv_x}{dt} \right]_{t - \frac{r}{c}}, \quad \cdots \quad (1)$$

and then the flow of energy through w' per unit of time will be

$$CE_x{}^2 w'$$

as far as this one component is concerned.

Since the motion of the electrons between the metallic atoms is highly irregular and of such a nature that it is impossible to follow it in detail, we must rather content ourselves with mean values of the variable quantities calculated for a sufficiently long interval of time. We shall, therefore, always consider only the mean values of our quantities taken over the large time between the instants $t = 0$ and $t = \theta$. For example, the flow of energy through w' is, on the average, equal to

$$cw'\frac{1}{\theta}\int_0^\theta \mathrm{E}_x{}^2 dt = c\overline{\mathrm{E}_x{}^2}w' \text{ say.}$$

Now whatever be the way in which E_x changes from one instant to the next, we can always expand it in a series by the formula

$$\mathrm{E}_x = \sum_{s=1}^\infty a_s \sin \frac{s\pi t}{\theta},$$

where s is a positive integer and

$$a_s = \frac{2}{\theta}\int_0^\theta \sin \frac{s\pi t}{\theta} \mathrm{E}_x dt.$$

The frequency in the sth term of this series is $\dfrac{s\pi}{\theta}$ so that the wave-length of the vibration represented in it is

$$\lambda = \frac{2c\theta}{s}.$$

If θ is very large the part of the spectrum corresponding to the small interval of length $d\lambda$ between wave-lengths λ and $\lambda + d\lambda$ will contain the large number $\dfrac{2c\theta}{\lambda^2} d\lambda$ of spectral lines represented by terms of this series.

If now we substitute the Fourier series for E_x into the expression for the mean energy flux through w', we shall find in the usual manner that it is equal to

$$c\overline{\mathrm{E}_x{}^2}w' = \tfrac{1}{2}cw' \sum_{s=1}^\infty a_s{}^2. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

To obtain the portion of this flux corresponding to wavelengths between λ and $\lambda + d\lambda$ we have only to observe that the $\dfrac{2c\theta}{\lambda^2} d\lambda$ spectral lines, lying within that interval, may be considered to have equal intensities. In other words, the value a_s may be regarded as equal for each of them, so that they contribute to the sum Σ in (2) an amount

$$\frac{2c\theta a_s{}^2 d\lambda}{\lambda^2} .$$

Consequently the energy flux through w' belonging to the interval of wave-lengths $d\lambda$ is given by

$$\frac{c^2\theta w' a_s{}^2 d\lambda}{\lambda^2},$$

and we now want to find a_s.

From the value of E_x given by equation (1) we see that

$$a_s = -\frac{1}{2\pi\theta c^2 r} \sum \left\{ e \int_0^\theta \sin\frac{s\pi t}{\theta} \frac{d[v_x]}{dt} \, dt \right\},$$

where the square bracket round the v_x serves to indicate the value of this quantity at the time $t - \dfrac{r}{c}$. The sign Σ now refers again to a sum taken over all the electrons in the part $w\Delta$ of the plate.

On integration by parts we find

$$a_s = \frac{se}{2\theta^2 c^2 r} \sum \int_0^\theta [v_x] \cos\frac{s\pi t}{\theta} dt,$$

or what is the same thing

$$a_s = \frac{se}{2\theta^2 c^2 r} \sum \int_{-\frac{r}{c}}^{\theta-\frac{r}{c}} v_x \cos\frac{s\pi}{\theta}\left(t + \frac{r}{c}\right) dt.$$

Now each of the integrals on the left is made up of two parts, arising respectively from the intervals between the consecutive impacts of the electrons and from the intervals during these impacts. If, as mentioned above, we can suppose the duration of an encounter of an electron with an atom to be very much smaller than the time between two successive encounters of the same electron, we may neglect altogether the part that corresponds to the collisions and confine ourselves entirely to the part corresponding to the free paths between the collisions. But while an electron travels over one of these free paths, its velocity v_x is constant. Thus the part of the integrals in a_s which corresponds to one electron and to the time during which it traverses one of its free paths is therefore

$$v_x \int_t^{t+\tau} \cos\frac{s\pi}{\theta}\left(t + \frac{r}{c}\right) dt,$$

where t is now the instant at which this free path is commenced and τ the duration of the journey along it; but this is equal to

$$\frac{\theta v_x}{s\pi}\left\{ \sin\frac{s\pi}{\theta}\left(t + \frac{r}{c} + \tau\right) - \sin\frac{s\pi}{\theta}\left(t + \frac{r}{c}\right) \right\}$$

$$= \frac{2\theta v_x}{s\pi} \sin\frac{s\pi\tau}{2\theta} \cos\frac{s\pi}{\theta}\left(t + \frac{r}{c} + \frac{\tau}{2}\right).$$

We now fix our attention on all the paths described by all the electrons under consideration during the time θ, and we use the symbol S to denote a sum relating to all these paths. We have then

$$a_s = \frac{se}{2\theta^2 c^2 r} \, \mathrm{S} \, \frac{2\theta v_x}{s\pi} \sin \frac{s\pi\tau}{2\theta} \cos \frac{s\pi}{\theta}\left(t + \frac{r}{c} + \frac{\tau}{2}\right).$$

We now want to determine the square of the sum S. This may be done rather easily because the product of two terms of the sum whether they correspond to different free paths of one and the same electron, or to two paths described by different electrons, will give 0 if all taken together. Indeed the velocities of two electrons are wholly independent of one another, and the same may be said of the velocities of one definite electron at two instants separated by at least one encounter. Therefore positive and negative values of v_x being distributed quite indiscriminately between the terms of the series S, positive and negative signs will be equally probable for the products of two terms. We have therefore only to calculate the sum of the squares of the terms in S or simply

$$\mathrm{S} \, \frac{4\theta^2 v_x^2}{s^2\pi^2} \sin^2 \frac{s\pi\tau}{2\theta} \cos^2 \frac{s\pi}{\theta}\left(t + \frac{r}{c} + \frac{\tau}{2}\right). \quad . \quad . \quad (3)$$

Now since the irregular motion of the electrons takes place with the same intensity in all directions, we may replace v_x^2 by $\frac{1}{3}v^2$. Also in the immense number of terms included in the sum (3) the quantities τ and v are very different, and in order to effect the summation we may begin by considering only those terms for which the product $\left(v \sin \dfrac{s\pi\tau}{2\theta}\right)$ has a certain value. In these terms which are still very numerous, the angle $\dfrac{s\pi}{\theta}\left(t + \dfrac{r}{c} + \dfrac{\tau}{2}\right)$ has values that are distributed at random over an interval ranging from 0 to $s\pi$. The square of the cosine may therefore be replaced by its mean value $\frac{1}{2}$, so that

$$a_s^2 = \frac{s^2 e^2}{24\theta^4 c^4 r^2} \, \mathrm{S}\left(\frac{4v^2\theta^2}{s^2\pi^2} \sin^2 \frac{s\pi\tau}{2\theta}\right),$$

or if we introduce, after Lorentz, the length of the path l instead of the time in it, this may be written

$$a_s^2 = \frac{s^2 e^2}{24\theta^4 c^4 r^2} \, \mathrm{S}\left(\frac{\sin\left(\dfrac{s\pi l}{2c\theta}\right)}{\dfrac{s\pi}{2c\theta}}\right)^2 \quad . \quad . \quad . \quad (4)$$

The metallic atoms being considered as practically immovable, the velocity of an electron will not be altered by a collision.   Let us, therefore, now fix our attention on a certain group of electrons moving along their zigzag lines with the definite velocity u.   Consider one of these electrons and let us calculate the chance of its colliding with an atom at rest in a unit of time.   This chance is obviously equal to the number of atoms in a cylinder of base πR^2 and height u, R being as before the sum of the radii of an atom and an electron ; it is therefore equal to

$$n\pi R^2 u,$$

n being the number of atoms per cubic centimetre in the metal.

But in unit time the electron under consideration travels a distance u, hence the chance of a collision of the electron with an atom per unit length of its path is

$$C = \frac{n\pi R^2 u}{u} = n\pi R^2,$$

and thus the mean free path of an electron is, as before,

$$l_m = \frac{1}{c} = \frac{1}{n\pi R^2} *.$$

It is important to notice for future reference that l_m is independent of u.   This is a consequence of the assumed rigidity of the atoms.

Now during the time θ one of the electrons moving with a velocity u describes a large number of paths, this number being given by

$$\frac{u\theta}{l},$$

and we now want to know how many of these paths are of given length l.

For this, let $f(l)$ be the probability that the electron shall describe a path at least equal to l, then $f(l+dl)$ is the probability that the electron has described a path l and shall describe a further distance dl, and this will necessarily be the product of $f(l)$ and another factor, this second factor expressing the probability of no collision occurring within

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* Lorentz does not make it clear that the l_m introduced here is, in fact, identical with that l_m used in the formula for the conductivity ; the expanded argument here given, however, proves directly what was probably already known to him.

the length dl. This factor is known from the above to be

$$(1-c) = \left(1 - \frac{1}{l_m}\right)$$

so that

$$f(l+dl) = \left(1 - \frac{1}{l_m}\right)f(l),$$

or what is the same thing

$$\frac{df}{dl} = -\frac{f}{l_m}$$

so that

$$f(l) = e^{-l/l_m},$$

the arbitrary constant of the integration being determined by the condition that $f(0)=1$.

Thus the probability of the electron describing a free path between l and $l+dl$ is expressed as the product of the probability that it has described a free path l, and that it will collide in the next small distance dl, and is therefore

$$e^{-l/l_m}\,cdl = \frac{1}{l_m}e^{-l/l_m}dl.$$

Thus of the total number of paths described by the electron in the time θ the number whose length lies between l and $l+dl$ is

$$\frac{u\theta}{l_m{}^2}e^{-l/l_m}dl,$$

so that the part of the sum in (4) contributed by these paths is

$$\frac{u\theta}{l_m{}^2}\left(\frac{\sin\left(\dfrac{s\pi l}{2\theta u}\right)}{\dfrac{s\pi}{2\theta u}}\right)^2 e^{-l/l_m}dl = u\theta e^{-l/l_m}\left(\frac{\sin\left(\dfrac{s\pi l_m}{2\theta u}\cdot\dfrac{l}{l_m}\right)}{\dfrac{s\pi l_m}{2\theta u}}\right)^2 dl.$$

On investigation of this expression from $l=0$ to $l=\infty$, we find the part of the sum in (4) due to one electron, which is therefore

$$\frac{u\theta}{\left(\dfrac{s\pi l_m}{2\theta u}\right)^2}\int_0^\infty \sin^2\left(\frac{s\pi l_m}{2\theta u}\cdot\frac{l}{l_m}\right)e^{-l/lm}dl = \frac{2u\theta l_m}{1+\dfrac{s^2\pi^2 l_m{}^2}{\theta^2 u^2}}.$$

Now the total number of electrons in the part of the metallic plate under consideration is $Nw\Delta$, and by Maxwell's

law, among these

$$4\pi N w \Delta \sqrt{\frac{q^3}{\pi^2}} e^{-qu^2} u^2 du$$

have velocities between u and $u+du$; the constant q is related to the velocity u_m already introduced above by the formula

$$q = \frac{3}{2u_m^2}.$$

Thus the total value of the sum in (4) is given by

$$4\pi N w \Delta \sqrt{\frac{q^3}{\pi^3}} \int_0^\infty \frac{2u\theta l_m}{1 + \dfrac{s^2\pi^2 l_m^2}{\theta^2 u^2}} e^{-qu^2} u^2 du$$

or, using $z = qu^2$, by

$$4 N w \Delta \sqrt{\frac{1}{\pi q}} \int_0^\infty \frac{z e^{-z} dz}{1 + \dfrac{s^2\pi^2 l_m^2 q}{\theta^2 z}}.$$

This integral cannot be evaluated in definite terms, being of the integral-logarithmic type, but we can obtain various good approximations to its value. In fact a direct use of the first theorem of mean values in the integral calculus soon shows that we have

$$\int_0^\infty \frac{z e^{-z} dz}{1 + \dfrac{s^2\pi^2 l_m^2 q}{z\theta^2}} = \frac{1}{1 + \dfrac{s^2\pi^2 l_m^2 q}{z_0 \theta^2}} \int_0^\infty z e^{-z} dz$$

$$= \frac{1}{1 + \dfrac{s^2\pi^2 l_m^2 q}{z_0 \theta^2}},$$

z_0 denoting some mean value of z, which is ultimately, however, a function of the one constant $\left(\dfrac{s^2\pi^2 l_m^2 q}{\theta^2} \right)$ in the integral; I find on trial that z_0 is such a function of this constant that its value lies between 1 and 2, the values it assumes for small and large values respectively of the constant. If, therefore, we define u_0 by the relation

$$q u_0^2 = z_0,$$

we shall know that u_0^2, ultimately a function of $\left(\dfrac{s^2\pi^2 l_m^2 q}{\theta^2} \right)$, must, however, lie between the limits

$$\tfrac{2}{3} u_m^2 \quad \text{and} \quad \tfrac{4}{3} u_m^2,$$

and then we shall have

$$a_s{}^2 = \sqrt{\frac{2}{3\pi}} \frac{s^2 e^2 l_m \mathrm{N} u_m w \Delta}{6\theta^3 c^4 r^2 \left(1 + \dfrac{s^2 \pi^2 l_m{}^2}{u_0{}^2 \theta^2}\right)},$$

and the expression for the partial energy flux through the element w' thus takes the form

$$\sqrt{\frac{2}{3\pi}} \frac{s^2 \mathrm{N} e^2 l_m u_m}{6\theta^2 c^2 r^2 \lambda^2} \cdot \frac{w w' \Delta d\lambda}{1 + \dfrac{s^2 \pi^2 l_m{}^2}{u_0{}^2 \theta^2}}.$$

But in virtue of the relation $\lambda = \dfrac{2c\theta}{s}$ this becomes

$$\frac{2}{3} \sqrt{\frac{2}{3\pi}} \frac{\mathrm{N} e^2 l_m u_m}{r^2 \lambda^4} \cdot \frac{d\lambda}{1 + \dfrac{4\pi^2 c^2 l_m{}^2}{u_0{}^2 \lambda^2}} \cdot \Delta w w'.$$

We therefore conclude that the emissivity of the plate is given by

$$\mathrm{E} = \frac{2}{3} \sqrt{\frac{2}{3\pi}} \frac{\mathrm{N} e^2 l_m u_m \Delta}{\lambda^4 \left(1 + \dfrac{4\pi^2 c^2 l_m{}^2}{u_0{}^2 \lambda^2}\right)}.$$

On combining the two expressions for E and A we find that

$$\mathrm{F}(\lambda, \mathrm{T}) = \frac{8\pi}{c} \frac{\mathrm{E}}{\mathrm{A}} = \frac{8\pi m u_m{}^2}{3\lambda^4} \cdot \frac{1 + \dfrac{32\pi}{3} \dfrac{c^2 l_m{}^2}{\lambda^2 u_m{}^2}}{1 + \dfrac{4\pi^2 c^2 l_m{}^2}{u_0{}^2 \lambda^2}},$$

which is exactly Lorentz's result if

$$\frac{u_0{}^2}{u} = \frac{3 u_m{}^2}{8},$$

$$u_0{}^2 = \frac{3\pi}{8} u_m{}^2,$$

a value which certainly lies within the above limits possible for $u_0{}^2$, but which can only be said to be satisfied exactly for one particular value of $\left(\dfrac{l_m}{\lambda}\right)$.

If, therefore, the formula adopted for σ is exact, our analysis verifies that Kirchhoff's law does not apply exactly in the case under investigation. Of course the discrepancy is small except perhaps for extremely short waves, but it is worth noticing.

It would, however, appear more probable that it is the formula for σ that is at fault* and not Kirchhoff's more general law, the truth of which can hardly be doubted. It is, however, in any case interesting to notice that although the formula for σ adopted above may not be exact, the formula necessitated by Kirchhoff's law in combination with the above analysis provides an interesting verification of its general form.

In any case, however, we may conclude that for all practical purposes the complete radiation formula applicable all along the spectrum is given by the usual Rayleigh-Jeans formula

$$F(\lambda, T) = \frac{8\pi m u_m^2}{\lambda^4},$$

as Lorentz predicts, a formula which is, however, only physically applicable in the extreme ultra-red part of the spectrum.

But this general conclusion is utterly absurd both from a mathematical and a physical point of view, and it therefore appears that some fundamental error has been committed either in the physical assumptions made or in the mathematical analysis based on these assumptions.

It is very difficult, if not quite impossible, to indicate any steps in the above analysis about whose mathematical rigour any doubts can be raised, but it is worth noticing that the final result obtained is not consistent with the preliminary assumptions, inasmuch as the Fourier series initially assumed, which can have no meaning unless it is convergent, ultimately turns out to be divergent, so that the theory would appear to lead to a result which is ultimately a contradiction in terms, or, at least, apparently so. Some light is, however, thrown on this question by an examination of the physical basis of the theory.

The one advantage possessed by the present form of theory over Lorentz's original form is that the number of physical assumptions on which it is based is reduced from two to one, so that it is now possible to determine the actual extent to which the physical basis of the theory is responsible for the result obtained. We have merely assumed that the duration of every collision of an electron with an atom is vanishingly small compared with the other periods involved in our analysis, and as long as this assumption is justified our result must be correct. But, as a matter of fact, in actual

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* This probability is fully borne out by a more detailed investigation of the question as to the proper expression for σ.

practice this assumption is justified only to a comparatively rough extent and only when all the other times involved in the analysis are large compared with the usual intra-molecular periods, so that the results obtained can only be applicable in the extreme ultra-red region of the spectrum, where it is of course known to apply. As soon as the encounters between the electrons and atoms are sufficiently long compared with the period of the light discussed, the effect of the collision will make itself felt in modifying the radiation formula, a conclusion drawn some time previously by J. J. Thomson.

It is just the assumption concerning the shortness of the collisions which is the predominating factor in restricting the general application of the Rayleigh-Jeans formula.

The fact that the general radiation formula which is to be applicable all along the spectrum must ultimately contain some general account of the actual collisions of the electrons with the atoms can be illustrated in various ways. Let us confine our attention to one of the free electrons in the metal considered in the above analysis ; the average flux of energy through w' arising as a result of its motion is

$$\frac{e^2 w'}{8\pi^2 c^3 r^2 \theta} \int_0^\theta \left(\frac{d[r_x]}{dt}\right)^2 dt = \frac{e^2 w'}{8\pi^2 c^3 r^2 \theta} \int_0^\theta \frac{d[v_x]}{dt} d[v_x].$$

Now if the collisions are all of short duration and $\Delta[v]$ denotes the total change in $[v]$ during a typical one of these collisions of total duration Δt, then the energy radiated through w' during this collision is of total amount

$$\frac{e^2 w'}{8\pi^2 c^3 r^2 \theta} \frac{\{\Delta[v_x]\}^2}{\Delta t},$$

which is inversely as Δt. Thus if, as in the above, we assume the duration of all the collisions to be infinitely short, the total amount of energy radiated away will be infinitely large. This merely means of course that as soon as the time of a collision becomes appreciable a closer investigation will be necessary, involving necessarily some account of the nature of the collision.

It is now no longer surprising that a divergent series is obtained in the expression for the total energy ; in fact the shorter the collisions the farther up the spectrum does the agreement between theory and practice hold, but then the bigger is the total energy.

These results are still further illustrated by the results of a general theory developed by Thomson [*] on molecular

* Phil. Mag. [5] xiv. p. 217 (1907).

kinetic principles. The method followed by Thomson is analogous to that of Lorentz, but it avoids the probability considerations involved in that author's theory. He views, with Lorentz, the radiation as a result of the changes of velocity produced in the collisions of the electrons against the molecules, and he concludes that the manner in which these changes take place must, as stated above, ultimately be of influence on the final formula for the radiation. Assuming, then, as possible arbitrary types of acceleration of an electron during a collision functions of the time of the form

$$\text{(I.)} \quad A e^{-\frac{t^2}{a^2}}, \qquad\qquad \text{(II.)} \quad \frac{A}{a^2 + t^2},$$

in which A and a are constants, he arrives at forms of $F(\lambda, T)$ of the following types respectively,

$$\text{(I.)} \quad F(\lambda, T) = \frac{8 m u_m{}^2}{3 \lambda^4} e^{-\frac{8 \pi^2 a^2}{\lambda^2}},$$

$$\text{(II.)} \quad F(\lambda, T) = \frac{8 m u_m{}^2}{3 \lambda^4} e^{-\frac{4 \pi c a}{\lambda}},$$

which give for the total energy radiated respectively

$$\text{(I.)} \quad \frac{8 m u_m{}^2}{3} \int_0^\infty e^{-\frac{8 \pi^2 a^2}{\lambda^2}} \frac{d\lambda}{\lambda^4} = \frac{8 m u_m{}^2}{3 a^3} \int_0^\infty e^{-8 \pi^2 x^2} x^2 \, dx,$$

and

$$\text{(II.)} \quad \frac{8 m u_m{}^2}{3} \int_0^\infty e^{-\frac{4 \pi c a}{\lambda}} \frac{d\lambda}{\lambda^4} = \frac{8 m u_m{}^2}{3 a^3} \int_0^\infty x^2 e^{-4 \pi c x} \, dx,$$

where in each integral on the right we have written $x = a/\lambda$.

Now in each of the two cases here illustrated the constant a turns out to be approximately equal to the time of duration of an encounter of an electron with an atom, so that if we assume this time to be infinitely small both forms of Thomson's theory agree in giving

$$F(\lambda, T) = \frac{8 m u{}^2}{\lambda^4}$$

as the complete radiation formula all along the spectrum, but in both cases the total energy is infinite of the order $(1/a^3)$. It would thus appear, both from these two examples and also from the more general case discussed above, that any general theory which leads to the Rayleigh-Jeans formula as the formula generally applicable all along the spectrum must involve some assumption which essentially implies that the total amount of energy radiated is infinite, so that it

cannot represent any real physical example of a radiating body of any known type. Physically this implies that the general restrictions limiting in actual practice the validity of the physical hypotheses on which the theory is based, must also limit the applicability of the formula obtained from the theory, an obvious remark which it appears, however, necessary to insist upon, because it is the expressed opinion of certain mathematical physicists that, for example, the Rayleigh-Jeans formula obtained by Lorentz on certain obviously restricted assumptions is of a general validity in no way limited by the restrictions naturally imposed on these assumptions. The results obtained by Thomson are almost conclusive evidence that this contention is in no wise justifiable, and the results of the above form of Lorentz's theory are also against such an opinion.

I hope to discuss, in further detail, in a future communication some of the points raised in the latter part of this paper and not fully disposed of.

The University, Sheffield,
  October 9, 1914.

Note added Dec. 2nd, 1914.—Since the above paper was sent to press I have discovered that Prof. H. A. Wilson has anticipated the main point of the above analysis although he apparently failed to appreciate its bearing (Phil. Mag. Nov. 1910). He, however, unfortunately includes it as a small part of a paper, all the other results of which are either incomplete or inaccurate, and I think it deserves better and more elaborate treatment. Some advantage may therefore be gained by amplifying the point as above.

XVIII. *On the Electron Theory of Metallic Conduction.*—I. *By* G. H. LIVENS [*].

Introduction.

ONE of the greatest successes achieved by the so-called theory of electrons has been in its application to the explanation of the details of the conduction of electricity in metals. Encouraged by the wonderful success of the earlier and more tentative applications of the theory by Drude and Riecke, numerous writers have endeavoured by the introduction of statistical methods to develop the theory in still greater detail. Many of the more fundamental results in

* Communicated by the Author.

the theory have thereby received verification and justification from several entirely independent investigations, although it must be admitted that some of the results of these investigations have not always been so happily coincident as one might desire. This remark applies particularly to the formula for the electrical conductivity which expresses it in terms of the electron constants of the metal. After Drude's initial attempt to deduce a formula for the conductivity, the problem appeared to be finally settled, at least as far as its application in the theory of steady currents, by the very general and elaborate investigations by Lorentz *. The formulæ obtained by Lorentz, however, appear to require modification and amplification in order to make them applicable for very rapidly alternating fields, particularly those associated with radiation. The application of the theory of electrons to these extensions, initiated by Thomson †, was fully carried out and in great detail by Jeans ‡ and H. A. Wilson §, their method of procedure being, however, essentially different from that followed by Lorentz. It appears, however, that the formula obtained for the conductivity by Wilson, who alone carries the calculation right through on the statistical basis, does not agree with Lorentz's formula in the limiting case, being in fact half as big again.

It is maintained by Nicholson ‖ that as far as the optical properties of metals are concerned Wilson's formula is more satisfactory than any other yet proposed. He also considers that Wilson's treatment is the most satisfactory yet published and that from the theoretical standpoint it is complete ! ¶

The object of the present communication is to prove that a rigorous treatment of the problem along the lines laid down by Wilson and Thomson leads to a formula differing from Wilson's by a factor 2/3, which is just what is required to make it consistent with Lorentz's result in the limiting case. There is a discrepancy in Wilson's treatment of the problem which has considerable bearing on the final result obtained.

The discussion of the actual bearing of the results of the present discussion on the optical side of the question will be reserved for a future communication, as it is merely desired to show that the principles underlying the discussions

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* Vide 'The Theory of Electrons.'   † Phil. Mag. Aug. 1907.
‡ Phil. Mag. June and July, 1909.   § Phil. Mag. Nov. 1910.
‖ Phil. Mag. Aug. 1911.
¶ Nicholson informs me that he has subsequently modified his views as to the exactness of the formulæ under dispute.

of Thomson and Wilson are consistent with Lorentz's general theory. It is perhaps necessary to add that Wilson gives two independent deductions of his formula, one following Jeans and the second following Thomson. It is the second deduction with which I shall here concern myself, the first, being more concerned with the optical side of the question, will be discussed in the future communication.

With each of the aforementioned authors we shall consider that the phenomenon of electrical conduction in the metal arises entirely from the motions of a swarm of electrons moving about in a perfectly irregular manner in the free space between the atoms of the metal, which are presumed to be of such comparatively large mass that their energy and motion may be neglected. The electrons and atoms are presumed to be perfectly elastic spheres so that the velocity of an electron is not altered by collision, the atom being at rest.

The general principles underlying the determination of the conductivity (σ) to be here reviewed, depend essentially on the fact that the energy dissipated by a steady current, driven by the electric force E, is presumed to be the same as the energy acquired by the electrons on account of the action on them of the electric force during their otherwise free motion between the collisions, and which is dissipated on the collision of the electron at the end of this path. The rate of dissipation is known to be σE^2, and it can be calculated by statistical considerations of the motions of the electrons.

We shall first make the calculation on the assumption that a steady field of constant strength E is in action parallel to a fixed direction. This is not precisely the problem discussed by Thomson and Wilson, but the analysis is much easier and has the additional advantage of bringing out very clearly the correction which it is necessary to introduce into the original analysis of these authors. The extension to rapidly alternating fields will be given in a subsequent paragraph.

Analysis for steady fields.

We choose a definite system of rectangular axes with the x-axis parallel to the direction of the electric force. Referred to these axes the velocity of the typical electron at time t has components which we shall denote by (ξ_t, η_t, ζ_t), so that the resultant velocity is r_t where

$$r_t^2 = \xi_t^2 + \eta_t^2 + \zeta_t^2$$

The equations of motion of the typical electron during its free motion between two collisions while under the action of the electric force is

$$m\frac{d\xi_t}{dt} = e\mathrm{E}, \quad m\frac{d\eta_t}{dt} = m\frac{d\zeta_t}{dt} = 0,$$

where m denotes the inertia mass of the electron and e the charge on it. Thus

$$\xi_t = \frac{e\mathrm{E}t}{m} + \xi, \quad \eta_t = \eta, \quad \zeta_t = \zeta,$$

(ξ, η, ζ) being the velocity at the instant of beginning the free motion from which the time is also measured. The work done by the electric field on this electron during the whole of the time between two impacts, an interval of length τ, is thus

$$\int_0^\tau e\mathrm{E}\xi_t dt = e\mathrm{E}\int_0^\tau \left(\frac{e\mathrm{E}t}{m} + \xi\right)dt$$
$$= \frac{\mathrm{E}^2 e^2}{m}\frac{\tau^2}{2} + e\mathrm{E}\xi\tau \; ;$$

and we now require the sum of the quantities of this type corresponding to all the free paths of all the electrons per unit of volume covered during the unit interval of time. Denoting this sum by S we find that the total amount of heat developed per unit time per unit volume is

$$\mathrm{H} = \sigma\mathrm{E}^2 = \mathrm{S}\left(\frac{\mathrm{E}^2 e^2}{m}\cdot\frac{\tau^2}{2} + e\mathrm{E}\xi\tau\right).$$

Thomson and Wilson both proceed by making a statement [*] which is equivalent in the present notation to saying that

$$\mathrm{S}(e\mathrm{E}\xi\tau) = 0,$$

their reason being presumably that since positive and negative values of ξ are equally probable there will be equal positive and negative terms in the sum which will thus on the whole be zero. This statement, however, does not appear to be quite correct, since, granted exactly identical conditions for electrons with the component velocity ξ, the value of τ is less when ξ is positive than when it is negative by an amount of the order $e\mathrm{E}\tau$, so that there must in any case be a residue

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[*] It is perhaps only fair to add that this statement, in the form I give it, probably never occurred to either author, since in the particular case they examine they have another plausible reason for neglecting the corresponding term of the sum.

in this term which is of the same order of magnitude as the other term of the sum actually retained.

The summation will be best effected if, after Lorentz, we interpret it in terms of the lengths of free paths and velocities in them instead of the time of duration. From the equations above we find that the projections of the particular path there under consideration along the co-ordinate axes are of lengths

$$l_x = \frac{e\mathrm{E}}{m} \cdot \frac{\tau^2}{2} + \xi\tau, \quad l_y = \eta\tau, \quad l_z = \zeta\tau,$$

so that the length of the path is practically

$$l^2 = l_x{}^2 + l_y{}^2 + l_z{}^2$$

$$= r^2\tau^2 + \frac{e\mathrm{E}}{m}\xi\tau^3,$$

where we use

$$r^2 = \xi^2 + \eta^2 + \zeta^2$$

and neglect squares of the small order term involving E. From this it is easy to see that to the same order of magnitude

$$\tau = \frac{l}{r}\left(1 - \frac{e\mathrm{E}\xi l}{2mr^3}\right),$$

so that the above expression for the work done by the electric field on the electron in its free path is to the same order of approximation

$$\frac{e^2\mathrm{E}^2 l^2}{2mr^2} + \frac{e\mathrm{E}\xi l}{r}\left(1 - \frac{e\mathrm{E}\xi l}{2mr^3}\right)$$

$$= \frac{e^2\mathrm{E}^2}{2m}\frac{l^2}{r^2}\left(1 - \frac{\xi^2}{r^2}\right) + \frac{e\mathrm{E}\xi l}{r},$$

so that we have to evaluate

$$\mathrm{H} = \mathrm{S}\left[\frac{e^2\mathrm{E}^2}{2m} \cdot \frac{l^2}{r^2}\left(1 - \frac{\xi^2}{r^2}\right) + \frac{e\mathrm{E}\xi l}{r}\right].$$

Wherein it is to be remembered that all velocities are to be taken at their initial value at the beginning of an impact.

Consider first the contribution to H made by a single electron which would in the absence of an electric field be moving freely with a velocity r, and which will therefore move so that it resumes this value at the beginning of each free path. This assumes with Thomson * that the whole

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* Wilson does not state that this assumption underlies his analysis, but without it his analysis is meaningless. It is, I believe, his failure to realise the importance of a clear definition of this point which is the cause of the errors he makes in the analysis.

effect impressed on an electron by the field during its motion before a collision is obliterated by the collision. During a unit of time this electron traverses a large number of free paths, this number being given by

$$\frac{r}{l_m},$$

where l_m is the mean length of a path. Of this number we know that there are a number

$$\frac{r}{l_m{}^2} e^{-l/l_m} dl$$

whose lengths lie between l and $l + dl$. These contribute to the above sum an amount

$$\frac{e^2 E^2}{2mr}\left(1 - \frac{\xi^2}{r^2}\right)\frac{l^2}{l_m{}^2} e^{-l/l_m} dl + e E \xi \frac{l}{l_m{}^2} e^{l/l_m} dl.$$

Integrating this expression from 0 to ∞ and noticing that ξ is not a function of l, we find the whole contribution to the sum S due to one electron in the form

$$\frac{e^2 E^2 l_m}{2mr}\left(1 - \frac{\xi^2}{r^2}\right) + e E \xi.$$

It is now clear that the mean free path l_m which was merely introduced in a general manner (much on the lines adopted by Lorentz in his book 'The Theory of Electrons,' page 282, note 36) can be assumed to have its undisturbed value, which it assumes in the absence of an electric field *.

This last expression must be summed over all the electrons in a unit volume. If, as above, we assume that each collision destroys the effects of the electric field, then we may assume that the distribution of the initial velocities among the electrons is that expressed by Maxwell's law ; in other words the number of electrons per unit volume with their velocities between the limits (ξ, η, ζ) and ($\xi + d\zeta$, $\eta + d\eta$, $\zeta + d\zeta$) is

$$N \sqrt{\frac{q^3}{\pi^3}} e^{-qr^2} d\xi \, d\eta \, d\zeta,$$

wherein N is the total number of electrons per unit volume

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* Some doubt may be expressed as to the general validity of the argument just repeated, but I think, on due consideration, it will be difficult to replace it by any other. Besides, the argument used by Lorentz to deduce the law of distribution of the lengths of path is probably independent of the action of the field, if l_m is properly interpreted.

and q is a constant which is connected with the mean square of the velocities, viz. u_m, by the relation

$$q = \frac{3}{2u_m{}^2}.$$

The contribution of this group of electrons to H is thus

$$d\mathrm{H} = \frac{\mathrm{N}e^2 l_m}{m}\sqrt{\frac{q^3}{\pi^3}}\left(1 - \frac{\xi^2}{r^2}\right)\frac{e^{-qr^2}}{r}\,d\xi\,d\eta\,d\zeta$$

$$+ e\mathrm{EN}\sqrt{\frac{q^3}{\pi^3}}\,e^{-qr^2}\xi\,d\xi\,d\eta\,d\zeta.$$

Integration of this expression over all positive and negative values of the variables (ξ, η, ζ) furnishes the complete value for H. The integral due to the second part of the expression obviously vanishes, and so we are left with

$$\mathrm{H} = \frac{\mathrm{E}^2\mathrm{N}e^2 l_m}{m}\sqrt{\frac{q^3}{\pi^3}}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\left(1 - \frac{\xi^2}{r^2}\right)\frac{e^{-qr^2}}{r}\,d\xi\,d\eta\,d\zeta.$$

To evaluate this we may, as usual, put ξ^2 equal to $\frac{1}{3}r^2$ and $d\xi\,d\eta\,d\zeta$ equal to $4\pi r^2 dr$, and then we find that

$$\mathrm{H} = \frac{4\pi\mathrm{N}e^2 l_m\mathrm{E}^2}{3m}\sqrt{\frac{q^3}{\pi^3}}\int_0^\infty 2re^{-qr^2}dr$$

$$= \left(\frac{4\mathrm{N}e^2 l_m}{3m}\sqrt{\frac{q}{\pi}}\right)\mathrm{E}^2$$

$$= 2\sqrt{\frac{2}{3\pi}}\cdot\frac{\mathrm{N}e^2 l_m}{mu_m}\,\mathrm{E}^2.$$

And since $\mathrm{H} = \sigma\mathrm{E}^2$ we see that

$$\sigma = 2\sqrt{\frac{2}{3\pi}}\frac{\mathrm{N}e^2 l_m}{mu_m},$$

which is precisely Lorentz's result.

Analysis for rapidly varying fields.

The ideas of the preceding analysis are directly applicable in the more general case of a rapidly alternating field such as we find associated with radiation. We may, for such a case, take the electric force E to be simple harmonic with a period p : say

$$\mathrm{E} = \mathrm{E}_0\cos(pt + \epsilon).$$

We have then the equations of motion of the typical electron in the form

$$m\dot{\xi}_t = e\mathrm{E}_0 \cos(pt+\epsilon) \quad \dot{\eta}_t = \dot{\zeta}_t = 0,$$

so that now

$$\xi_t = \frac{e\mathrm{E}_0}{mp}\left\{ \sin(pt+\epsilon) - \sin\epsilon \right\} + \xi,$$

$$\eta_t = \eta, \qquad \zeta_t = \zeta,$$

and also the projections of the typical free path along the three coordinate axes are of lengths

$$l_x = \xi\tau + \frac{e\mathrm{E}_0}{mp^2}\left\{ \cos\epsilon - \cos(p\tau+\epsilon) - p\tau \sin\epsilon \right\},$$

$$l_y = \eta\tau, \qquad l_z = \zeta\tau,$$

and thus to the usual order of approximation we have the length of the path given by

$$l^2 = r^2\tau^2 + \frac{2\xi e\mathrm{E}_0\tau}{mp^2}\left\{ \cos\epsilon - \cos(p\tau+\epsilon) - p\tau \sin\epsilon \right\},$$

and again

$$r\tau = l\left[1 - \frac{e\mathrm{E}_0\xi}{mp^2rl}\left\{ \cos\epsilon - \cos(p\tau+\epsilon) - p\tau \sin\epsilon \right\}\right].$$

In this case the work done by the electric field during the particular free path under consideration is

$$\int_0^\tau e\mathrm{E}_0 \cos(pt+\epsilon)\xi_t dt$$

$$= \int_0^\tau e\mathrm{E}_0 \cos(pt+\epsilon)\left\{ \frac{e\mathrm{E}_0}{mp}\left[\sin(pt+\epsilon) - \sin\epsilon \right] + \xi \right\} dt$$

$$= \frac{e^2\mathrm{E}_0^2}{2mp^2}\left\{ \sin(p\tau+\epsilon) - \sin\epsilon \right\}^2$$

$$+ \frac{\xi e\mathrm{E}_0}{mp}\left\{ \sin(p\tau+\epsilon) - \sin\epsilon \right\}.$$

This expression is again better interpreted in terms of the length of free path and the velocity in it. On substitution therefore of the value of τ from above we find that to the second order in E^2 this expression is equal to

$$\frac{e^2\mathrm{E}_0^2}{2mp^2}\left[\left\{ \sin\left(\frac{pl}{r}+\epsilon\right) - \sin\epsilon \right\}^2 \right.$$

$$- \frac{2\xi^2}{r^2}\cos\left(\frac{pl}{r}+\epsilon\right)\left\{ \cos\epsilon - \cos\left(\frac{pl}{r}+\epsilon\right) - \frac{pl}{r}\sin\epsilon \right\}$$

$$\left. + \frac{\xi_0 e\mathrm{E}_0}{mp}\left[\sin\left(\frac{pl}{r}+\epsilon\right) - \sin\epsilon \right]. \right.$$

And we must now sum this expression over all the free paths of all the electrons per unit volume per unit time. We may notice, however, that since the phase ϵ of the electric force at the beginning of the path may have any value whatever, we may at once replace all factors involving ϵ by their mean values. For example, the mean value of

(i.) $\cos^2\left(\dfrac{pl}{2r}+\epsilon\right)$ is $\dfrac{1}{2}$;

(ii.) $\cos\left(\dfrac{pl}{r}+\epsilon\right)\cos\epsilon$ is $\dfrac{1}{2}\cos\dfrac{pl}{r}$;

(iii.) $\cos^2\left(\dfrac{pl}{r}+\epsilon\right)$ is $\dfrac{1}{2}$;

(iv.) $\cos\left(\dfrac{pl}{r}+\epsilon\right)\sin\epsilon$ is $-\dfrac{1}{2}\sin\dfrac{pl}{r}$;

and the others are all zero.

We have thus to sum expressions referring to each free path of the type

$$\frac{e^2\mathrm{E}_0{}^2}{2mp^2}\left[2\sin^2\frac{pl}{2r}-\frac{\xi^2}{r^2}\left\{\cos\frac{pl}{r}-1+\frac{pl}{r}\sin\frac{pl}{r}\right\}\right].$$

Now, as before, let us confine our attention to one particular electron which in the absence of any external field would continue to move with velocity r, and which therefore will begin to describe each path with this velocity. In unit time this electron will describe on the average the number r/l_m of free paths, and of this number there are

$$\frac{r}{l_m{}^2}e^{-l/l_m}dl$$

whose length lies between l and $l+dl$. The contribution of these terms to the above sum is therefore

$$\frac{e^2\mathrm{E}_0{}^2}{2mp^2}\left[2\sin^2\frac{pl}{2r}\left(1+\frac{\xi^2}{r^2}\right)-\frac{\xi^2 pl}{r^3}\sin\frac{pl}{r}\right]\frac{r}{l_m{}^2}e^{-l/l_m}dl.$$

On integration of this expression from 0 to ∞ we find the whole contribution by this particular electron. Noticing that

$$\int_0^\infty \sin^2\frac{pl}{2r}e^{-l/l_m}dl=\frac{\dfrac{p^2 l_m{}^3}{2r^2}}{1+\dfrac{p^2 l_m{}^2}{r^2}},$$

and that

$$\int_0^\infty \frac{pl}{r}\sin\frac{pl}{r}e^{-l/l_m}\,dl = \frac{\dfrac{2p^2 l_m{}^3}{r^2}}{1+\dfrac{p^2 l_m{}^2}{r^2}},$$

we find that the contribution by the one electron to the total sum is

$$\frac{e^2 E_0{}^2 l_m}{2rm}\cdot\frac{1-\dfrac{\xi^2}{r^2}}{1+\dfrac{p^2 l_m{}^2}{r^2}}.$$

The number of electrons per unit volume with initial velocities in the limits between (ξ, η, ζ) and $(\xi+d\xi, \eta+d\eta, \zeta+d\zeta)$ is, as before,

$$N\sqrt{\frac{q^3}{\pi^3}}e^{-qr^2}\,d\xi\,d\eta\,d\zeta,$$

so that the contribution of these electrons to the total energy dissipated is

$$\frac{Ne^2 l_m E_0{}^2}{2m}\cdot\sqrt{\frac{q^3}{\pi^3}}\cdot\frac{1-\dfrac{\xi^2}{r^2}}{1+\dfrac{p^2 l_m{}^2}{r^2}}\frac{e^{-qr^2}}{r}\,d\xi\,d\eta\,d\zeta,$$

and again integrating over all possible values of (ξ, η, ζ) we find the total value of H in this case to be

$$H=\frac{4\pi}{3}\frac{Ne^2 l_m E_0{}^2}{m}\sqrt{\frac{q^3}{\pi^3}}\int_0^\infty\frac{e^{-qr^2}r\,dr}{1+\dfrac{p^2 l_m{}^2}{r^2}}.$$

Now the mean value of σE^2 is $\frac{1}{2}\sigma E_0{}^2$, so that on comparison we find that

$$\sigma=\frac{8\pi}{3}\frac{Ne^2 l_m}{m}\sqrt{\frac{q^3}{\pi^3}}\int_0^\infty\frac{e^{-qr^2}r\,dr}{1+\dfrac{p^2 l_m{}^2}{r^2}},$$

or put $s=qr^2$ and $p=\dfrac{2\pi c}{\lambda}$: we get

$$\sigma=\frac{4}{3}\frac{Ne^2 l_m}{m}\sqrt{\frac{q}{\pi}}\int_0^\infty\frac{e^{-s}\,ds}{1+\dfrac{4\pi^2 c^2 l_m{}^2 q}{\lambda^2 s}}$$

$$=2\sqrt{\frac{2}{3\pi}}\frac{Ne^2 l_m}{mu_m}\int_0^\infty\frac{e^{-s}\,ds}{1+\dfrac{6\pi^2 c^2 l_m{}^2}{\lambda^2 u_m{}^2 s}}.$$

This is the same result as obtained by Wilson, reduced, how-
ever by the factor 2/3 which brings it into line with the
result obtained by Lorentz, and which must be applicable
to the present problem in the limiting case of very long
waves.

Conclusion.

It would thus appear that a rigorous treatment of the
problem of conduction based on the above-mentioned ideas
leads to a formula which is entirely consistent with the results
of the analysis on more general lines given by Lorentz.
The two methods of reasoning appear at first sight to be
independent. Lorentz bases his calculations on the existence
of an average steady state of motion, in which the law of
distribution of the velocities among the electrons, which
differs from Maxwell's well known law owing to the action
of the electric field, is definitely calculable by similar
statistical considerations of the effect of the collisions. On
the other hand, Thomson and Wilson merely assume that the
whole effect imparted by the field to the electron in its
motion along a free path is destroyed by the collision at the
end of the path, so that the electron starts off each path with
the velocity which it would have according to Maxwell's
formula. which is presumed to hold in the absence of the ex-
ternal field. The two forms of the theory are thus mutually
consistent, and the fact that they lead to the same formula
for the conductivity is very strong evidence in favour of the
formula.

But the two views are probably much the same in the end,
although that of Lorentz is probably the more general. In
fact it is impossible to imagine the existence of an average
steady state, as Lorentz imagines, unless some such action as
that implied in Thomson's assumption is in play. Lorentz *
himself clearly appreciates the force of this remark and has
made various suggestions in explanation of it, so that it does
not appear necessary for me to go into further details. I
hope, however, to be able to return to it in a further com-
munication.

The University, Sheffield.
        Oct. 1914.

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* See *Vorträge über die Kinetische Theorie der Materie u. der Elek-
trizität* (Leipzig, 1914), p. 187.

XIX. *On the Plastic Bending of Metals.* *By* F. LLOYD HOPWOOD, *B.Sc., A.R.C.Sc., Demonstrator of Physics, St. Bartholomew's Hospital Medical College, London* *.

IF a uniform straight rod, clamped at one end and not otherwise supported, is allowed to sag from a horizontal position under the influence of its own weight, one of three things will happen:—

- *a.* It will quickly take up an equilibrium position in which the external forces are balanced by internal *elastic* forces, or
- *b.* Plastic yielding will occur and the sag will steadily increase with time, the rod coming SLOWLY to rest ultimately in an approximately vertical position, or
    (If the ratio of the length of the rod to its diameter exceeds a certain critical value)
- *c.* The plastic yielding will take place so rapidly that owing to its momentum the rod will bend until its free end passes below the clamp and oscillates about a point below the clamp. (See fig. 1.)

Fig. 1.
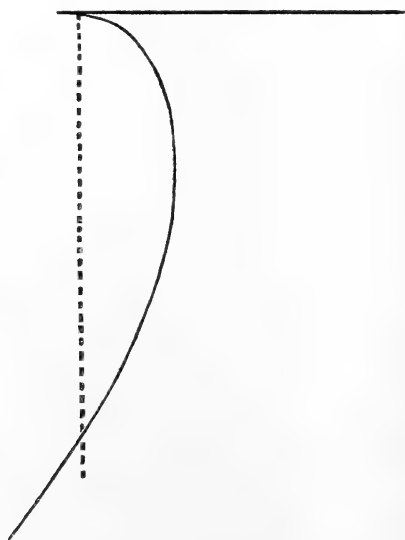
The complete mathematical theory of Case *a* is worked out in treatises on Elasticity.

Cases *b* and *c* involving as they do finite flexure and plastic yielding, under what is, in effect, a travelling load, are

incapable of exact mathematical treatment, and even an approximate theory presents almost insuperable difficulties *.
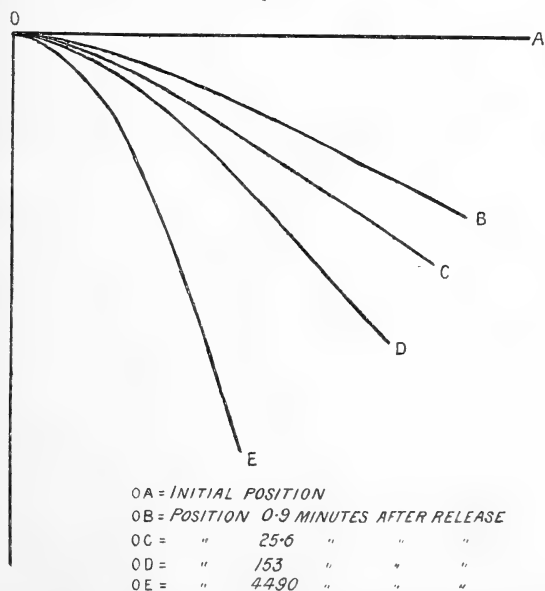
The present writer has obtained some empirical results for Case *b*, which, in the absence of other information, seem to him of sufficient interest to justify their publication.

The measurements here recorded were made on thin wires of commercially pure lead, but similar results have been obtained with thin wires of tin and cadmium. The lead wires were specially drawn for the experiment and were kept straight and not wound on bobbins. They were laid aside for several months at ordinary temperatures for annealing purposes.

Observations were made as follows :—

A suitable length of wire, having one end fixed in a horizontal clamp, was gently released by hand from the horizontal position at a known instant. A number of whole-plate photographs of the specimen, a vertical plumb-line, and the recording timepiece, were taken at times extending in some cases over several days. The photographs were taken against a black background, and accurate measurements of the coordinates of any point on the specimen were

Fig. 2.

OA = *INITIAL POSITION*
OB = *POSITION 0·9 MINUTES AFTER RELEASE*
OC =   "   25·6   "   "   "
OD =   "   153   "   "   "
OE =   "   4490   "   "   "

obtained by laying the developed plate on squared paper and inspecting with a low-power microscope. Fig. 2 shows the

* *Vide* Math. and Physical Papers of Sir G. Stokes, vol. ii. p. 178.

progressive yielding of the specimen referred to in Table I.
the curves being plotted from measurements made on the
photographs.

Taking the origin at the edge of the clamp and the hori-
zontal and vertical directions as the axes of x and y respec-
tively, it is found, on plotting the measurements from any
single photograph, that log x and log y are linear over a
considerable range, that is x and y are connected by a relation
of the form

$$x = ay^n. \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(A)}$$

In fig. 3, log x and log y are plotted for the whole rod for
several photographs of the same specimen.

Fig. 3.
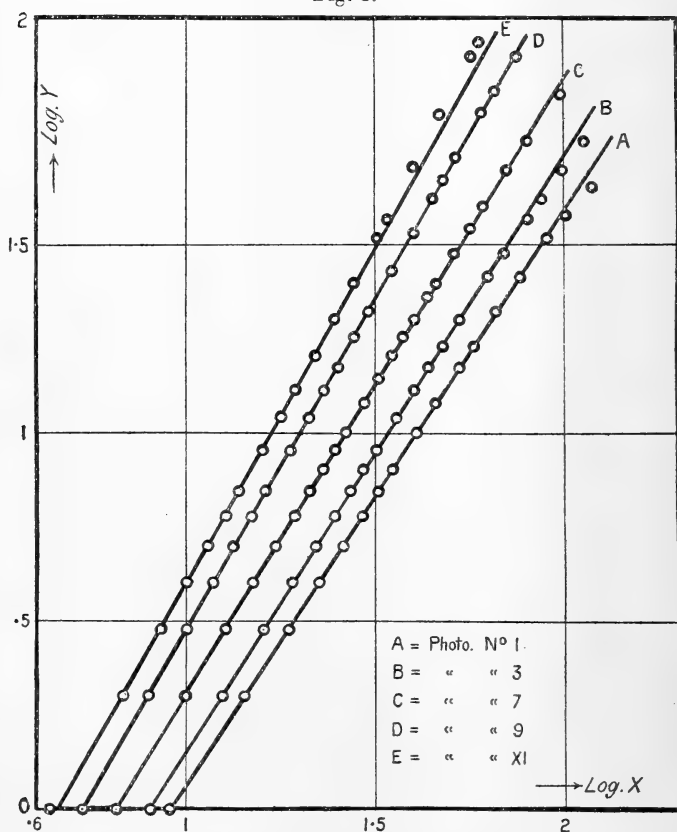
It is interesting to note that the divergences from linearity
which are shown by points remote from the clamp in the

earlier photographs are inclined in the opposite sense to those for later photographs.

Table I. gives complete particulars of a set of eleven photographs taken during the sagging of a single specimen, while Table II. shows the agreement between the observed values of x and those calculated from equation (A) for one of these photographs (number seven).

<div align="center">TABLE I.</div>

Lead Wire.   Length $= 11{\cdot}05$ cm.   Diameter $= {\cdot}023$ cm.
Lead began to sag July 21 at $12^{\text{h}}\ 35^{\text{m}}\ 49{\cdot}5^{\text{s}}$ p.m.

	Time in Minutes.	a.	n.	Temp.	Remarks.
First Photo taken July 21 at $\begin{smallmatrix}\text{h}\ \ \ \text{m}\ \ \ \text{s}\\12\ 36\ 44\end{smallmatrix}$	·90	9·44	·638	18·2° C.	
Second ,, ,, ,, 12 38 16	2·43	9·01	·636	18·2	
Third ,, ,, ,, 12 48 21	12·52	7·90	·634	18·1	
Fourth ,, ,, ,, 1 1 29	25·65	7·53	·627	18·1	
Fifth ,, ,, ,, 1 40 57	65·2	7·08	·616	18·2	
Sixth ,, ,, ,, 2 46 36	131	6·50?	·612	18·1	Faint plate.
Seventh ,, ., ,, 3 8 43	153	6·54	·606	18·1	
Eighth ,, ,, ,, 5 2 3	266	6·13	·600	18·2	
Ninth ,, ,, July 22 at 10 12 29	1296	5·26	·580	17·8	
Tenth ,, ,, July 23 at 2 25 3	2990	4·81	·571	16·9	
Eleventh ,, ,, July 24 at 3 25 18	4490	4·59	·566	18·2	

<div align="center">TABLE II.</div>

y.	x observed.	x calculated.	y.	x observed.	x calculated.
0...	0	0	17...	36·35	36·41
1..	6·5	6·54	18...	37·65	37·69
2 ..	10·0	9·95	19...	38·9	38·95
3...	12·75	12·73	20...	40·05	40·18
4...	15·15	15·15	21...	41·3	41·39
5...	17·3	17·34	22...	42·5	42·57
6...	19·4	19·37	23...	43·7	43·73
7...	21·3	21·27	24...	44·8	44·87
8...	23·1	23·08	25...	45·95	46·00
9...	24·8	24·77	26...	47·1	47·10
10...	26·5	26·40	27...	48·15	48·19
11...	28·0	27·97	30...	51·4	51·47
12...	29·6	29·48	35...	56·55	56·40
13...	31·0	30·95	40...	61·45	61·16
14...	32·3	32·52	50...	70·8	70·01
15...	33·75	33·75	60...	80·2	78·19
16...	35·05	35·10	*79·55	*98·2	92·76

<div align="center">* Coordinates of extremity.</div>

The calculated values of x given in the above table were obtained from the equation

$$x = 6 \cdot 54\, y^{\cdot 606}.$$

Both the quantities a and n of equation (A) are functions of the time which has elapsed since sagging began, a showing a big percentage variation and n a comparatively small variation, during a complete run.

The relation between a and time of sag is accurately expressed by the equation [*]

$$a = \alpha - \beta \log t. \quad . \quad . \quad . \quad . \quad . \quad \text{(B)}$$

This is clearly shown in fig. 4.

Fig. 4.
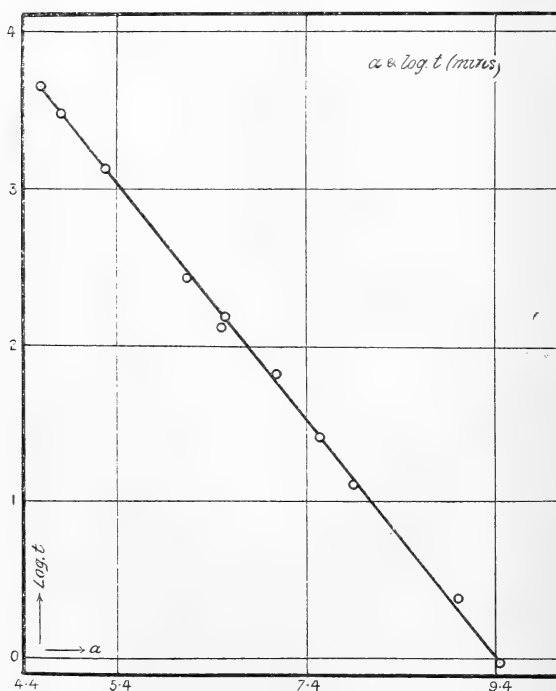
The approximate values of α and β are

$$\alpha = 9 \cdot 38, \quad \beta = 1 \cdot 311.$$

The result (B) is of some importance, for it is of the same

* Equation (B) obviously cannot hold from the instant sag commences.

form as that obtained by P. Phillips [*], connecting the extension with the time a metal wire is subject to a constant pull, and by C. E. Larard [†], connecting the torque and time when a metal is twisted to destruction at contant angular velocity.

In the light of their experiments, we may assume that the particular length of the specimen over which equation (A) is true coincides roughly with that in which plastic deformation is taking place, the remaining portion of the rod not being stressed beyond its elastic limit and acting merely as a load.

Fig. 5 shows that n is a parabolic function of the time

Fig. 5.
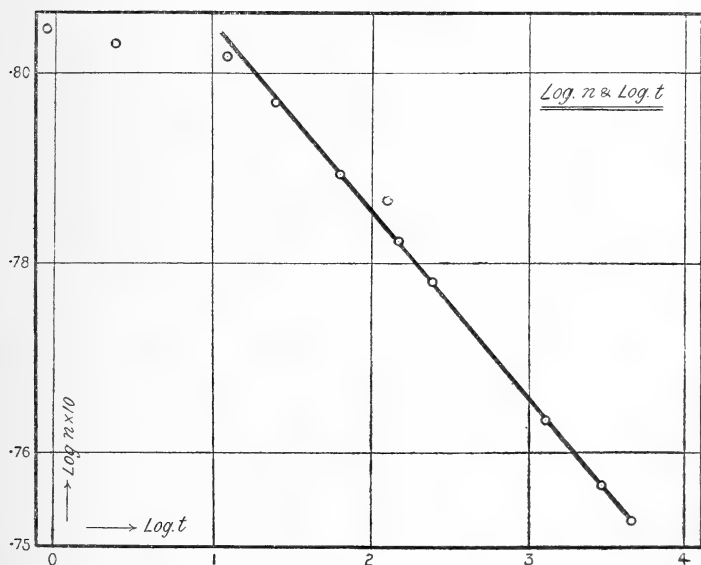
after an initial stage—taking about 15 minutes in present case—is passed.

For all the specimens on which the writer has experimented the value of n is in the neighbourhood of one half. This is rather suggestive of the well known Parabolic Catenary, in which the load on any element is proportional to the

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[*] P. Phillips, "On the Slow Stretch in Rubber, Glass, and Metals when subject to a Constant Pull," Phil. Mag. ix. (1905).

[†] C. E. Larard, "On the Law of Plastic Flow," Proc. Phys. Soc. 1913.

horizontal projection of the element. The slight variation of n with time may be ascribed to the rotation of the specimen as a whole about a horizontal axis through the origin.

Summary.

The sagging of thin uniform rods in the form of cantilevers under the influence of their own weight is divided into three cases, and empirical results are given for one of these cases.

The case considered is that in which plastic yielding occurs and the momentum generated in the rod is insufficient to cause it to swing past, and oscillate about, its final equilibrium position.

It is shown that for the thin wires used (lead, tin, and cadmium), if the origin be taken at the encastré end, the equation to the curve they assume is of the form $x = ay^n$.

The significance of the terms a and n is discussed.

XX. *On the Shape of small Drops of Liquid.*

To the Editors of the Philosophical Magazine.

Gentlemen,—

IN the November number of the Philosophical Magazine Mr. J. Rice puts forward a theory to account for the peculiar shape (a biconcave disk with rounded edges) of the red corpuscles of blood and of suspended particles in a lecithin emulsion. Now experiment shows that small particles of liquid suspended in another liquid always assume a spherical shape—as is to be expected from considerations of surface-tension. Hence the most natural explanation of the above shape is that the effect of surface-tension is modified by some other factor or factors. Mr. Rice, however, assumes that the peculiar shape is due to surface-tension, and attributes the deviation from sphericity to the smallness of the particle and consequent variability of the surface-tension. Assuming that the surface-tension T at any point is a function of the thickness of the disk at that point, Mr. Rice

calculates that the shape of particle for which the value of the integral

$$\iint T dS,$$

taken over the surface S of the particle, is a minimum.

The fallacy of the above method lies in the assumption that the above integral represents the " surface-energy." At the beginning of his mathematical treatment of the subject, Mr. Rice writes: " Now let T be the surface-tension or surface-energy per unit area of the interface "—a sentence in which the fundamental error is tacitly introduced. This identification of surface-tension with surface-energy per unit area is allowable only so long as the surface-tension is constant. The surface-tension is the *rate of increase* of the free energy with the area of the surface. If the area S of a film is increased by external forces from S_1 to S_2 the work done is

$$\int_{S_1}^{S_2} T dS,$$

which is equal to the change of free energy of the film. If the film is so thick that T is independent of S, the above expression becomes

$$T(S_2 - S_1).$$

Hence in this case the variation of the quantity TS is equal to the variation of the free energy, so that T may be called the " surface-energy per unit area of surface "*. When the film is so thin that T is a function of the thickness (*i. e.* of the area), it is as incorrect to call the surface-tension the " surface-energy per unit area of surface " as to call the pressure of a gas the " negative volume-energy per unit volume," or the tension of a spring the " elastic energy per unit extension."

The fact that a blood corpuscle is not spherical simply shows that it cannot be regarded as a drop of liquid suspended in another liquid. The occurrence of factors modifying simple surface-tension effects is quite common even outside the sphere of biology. A familiar instance is the formation of a soap layer at the interface between an alkaline solution and a vegetable or animal oil. This makes possible the formation of long thin cylinders of solution in the oil, which do not break up into drops till exceedingly thin—a process impossible in ordinary cases.

<div align="right">

Yours faithfully,

S. A. Shorter.

</div>

The University, Leeds.
26th Nov. 1914.

* Or more precisely "*free* surface-energy......"

XXI. *A Study of the Absorption Spectra of Organic Substances in the Light of the Electron Theory. By* N. P. K. J. O'N. McCleland, *B.A., Pembroke College, Cambridge* *.

[N.B.—The small numbers refer to the table of references given at the end.]

THE large number of experimental results now available has made it possible to trace a qualitative, and quite empirical relation between the constitutions of organic substances and their absorption spectra. Thus, it has been found that certain groupings of atoms are likely to give rise to bands in particular regions of the spectrum, but all theories which have hitherto been proposed to explain this fact appear to have postulated a characteristic type of vibration within each kind of group. Thus in the isorropesis theory of Baly a vibration between the forms

$$-CH_2 . C{=}O \rightarrow -CH{=}C-OH$$
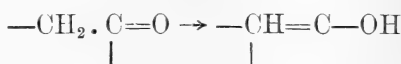
was suggested in the ketones, and between

$$\begin{array}{cc} C{=}O & C-O \\ | & \rightarrow \| \quad | \\ C{=}O & C-O \end{array}$$
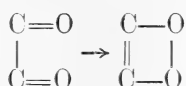
in the diketones, and so on. The only generally accepted law was that selective absorption in the ordinarily examined region † originates in the unsaturated condition of atoms, and that the accumulation of these unsaturated valencies shifts the absorption towards the red end of the spectrum.

In this paper a theory is proposed which, starting from the atom, builds up the spectrum in a perfectly general way and makes it possible to predict the positions of absorption bands with reasonable accuracy from the constitution, given certain fundamental constants. At present, these have only been obtained in a few cases owing to the lack of necessary data, and the author is unable to obtain these for want of a spectroscope.

* Communicated by Sir J. J. Thomson, O.M., F.R.S.

The author being under orders for active service has been obliged to leave some points in this paper unfinished, for example an extended table of numerical results might have been given. It is hoped that these deficiencies may be made up in the future.

† Until recently spectroscopes in general use covered the region $\lambda 600-230$ $(\mu\mu)$. Stark and his collaborators have lately published results down to $\lambda 180$. (See below.)

The model of the atom from which the results are obtained is that in which the valency electrons are supposed to move in circular orbits round a central nucleus; when the valencies become saturated, the corresponding electrons are supposed to be withdrawn out of their original orbits, perhaps into one of greater radius (about the line joining the nuclei) the periods in which are much greater than in the original. On this hypothesis, it is clear that when an atom is unsaturated as to one primary valency like the carbons in ethylene, there will remain one electron only in the outer orbit. If, now, a disturbing force such as light passes through the system, the electrons will vibrate about their orbits, and, from what has been said above, it appears that the periods of primary electrons of some of the commoner atoms happen to lie in or near the region examined in the ordinary instruments. The case when there is one such seat of disturbance has been fully dealt with by Drude [1] and others ; here cases where several such " vibration centres " occur in the molecule will be dealt with.

Since an electron moving in an orbit is a current, the vibrations of one will affect those of another in accordance with the laws of electrodynamics (see Appendix) ; the problem is therefore reduced to compounding vibrations by means of the mutual induction method.

It is not of course claimed that the whole of the mathematical treatment is original : it is, however, claimed that most of the cases worked out are new, and that this method has not been applied to the problem before.

There are, however, certain sources of uncertainty : in the first place the work is so complicated that only the simplest cases, *i. e.* those in which there is a certain amount of symmetry, are profitably discussed ; we assume, therefore, that slight changes not involving the introduction of a fresh vibration centre will not make any difference to the *type* of spectrum.

Again, there are on our theory several rings of electrons in a molecule, and these will all have some influence on one another. But while every electron in the molecule vibrates in a complex manner compounded of all possible periods, the most marked periods will be those which most closely approach the natural period of the electron in question. The effect of the other rings may explain the fine lines into which broad bands occasionally split under favourable conditions. In connexion with this it must be observed that the convenient abbreviation that " the band at (say) λ 300 is due to oxygen in the carbonyl group " does not

mean that it is due to vibrations of the electrons of free oxygen valencies alone, though these may contribute the greater part of the effective absorbing power. Further, the introduction of fresh vibration centres is bound to affect the induction constants of those already present by altering the relative positions of the orbits. These difficulties do not greatly disturb the qualitative results, but introduce an uncertainty into the values of the constants which can only be overcome by accumulation of experimental results, especially in regions of the spectrum which have recently been made available by Schumann.

There are two kinds of motion possible for the electrons, namely, in the plane of the orbit, and perpendicular to it. There are also two kinds of absorption : the one is observed in comparatively dilute solutions, very thin films or short columns of vapour, the other [2] through considerable thicknesses of pure substance. It is likely that these two kinds correspond to the two kinds of vibration. There are reasons for thinking that the first kind, which alone is dealt with here, depends on the vibrations in the plane.

In the numerical part of the paper, since the data cover only a small part of the spectrum it is impossible to obtain sufficient equations to give all the unknowns. We are therefore obliged to make some assumptions as will appear.

Notation and Units.

l represents coefficient of self-induction, or apparent mass, m and sometimes f, g, ϕ of mutual induction. r the friction of damping. c the stability. $\mathrm{E}e^{\iota pt}$ is the disturbing periodic force of the light.

The unit of time is so chosen that when the wave-length is in $\mu\mu$, $p = \dfrac{1}{\lambda} \times 100$.

l is assumed to be the same for all electrons and is taken as 1.

m and c vary for different atoms, the former also depending to some extent on the constitution of the molecule.

For example, the mutual induction between two atoms is increased when there is a mass of unsaturation outside them, $e.$ $g.$ the mutual induction between the $N =$ in $MeN = N - Me$ is less than that in the case of $C_6H_5 - N = N - C_6H_5$. This is readily explained as due to the repulsion of the unsaturated electrons in the phenyl groups forcing those of the nitrogens closer together.

Bands are spoken of as on the near or remote side of one another with reference to the red end of the spectrum.

The data refer as far as possible to alcoholic solutions, these being most abundant.

I. *One vibration centre only.*

This is the case developed by Drude [1].

The fundamental equation of motion may be put in the form

$$l\ddot{x} + r\dot{x} + cx = Ee^{\iota pt}. \quad \ldots \quad \text{(i.)}$$

If we assume $x = Xe^{\iota pt}$ for steady motion, we find

$$X(lp^2 - r\iota p - c) = -E \quad \ldots \quad \text{(ii.)}$$

giving X. The development of this is well known ; in particular it appears that the frequency of free vibration, corresponding to that of the ray most strongly absorbed, and so to the *head of the band*, is given by

$$-lp^2 + c = 0, \quad \ldots \quad \ldots \quad \text{(iii.)}$$

and also that the sharpness of the band depends on the smallness of $\dfrac{r^2 c}{l}$.

The only substances belonging to this type that have been examined are the aliphatic iodides [24]. The I vibration centre gives rise to a band at about $\lambda\,252$.

In what follows, the cases where there are several vibration centres will be treated as follows :—

First, the " frequency " equation (corresponding to (iii.)) will be investigated to find the positions of the heads of the bands, then in a few cases the "characteristic" equation (corresponding to (ii.)) will be examined to determine their nature.

II. *Two vibration centres.*

The equations of motion are

$$\left. \begin{array}{l} l_1\ddot{x} + m_1\ddot{y} + r_1\dot{x} + c_1 x = Ee^{\iota pt} \\ m\ddot{x} + l_2\ddot{y} + r_2\dot{y} + c_2 y = Ee^{\iota pt}, \end{array} \right\} \quad \ldots \quad \text{(iv.)}$$

assuming the relation

$$m_{12} = m_{21} = m.$$

The frequency equation is

$$(l_1p^2 - c_1)(l_2p^2 - c_2) = m^2p^4, \quad . \quad . \quad . \quad (\text{v.})$$

and, as is well known, the roots of this, *i.e.* the frequencies, lie outside those of the simple vibrations of each centre, *i. e.*, the bands are forced apart.

The characteristic equation for the X vibration centre is

$$\begin{aligned}X[(l_1p^2 - r_1\iota p - c_1)(l_2p^2 - r_2\iota p - c_2) - m^2p^4] \\ = -E[(l_2-m)p^2 - r_2\iota p - c_2]. \quad . \quad (\text{vi.})\end{aligned}$$

This is much too complicated to deal with conveniently, but in the symmetrical case we easily find the frequencies $p^2 = \dfrac{c}{l \pm m}$ and the characteristic equation becomes

$$X[(l+m)p^2 - r\iota p - c] = -E. \quad . \quad . \quad (\text{vii.})$$

When $p^2 = \dfrac{c}{l+m}$ we see the actual value of X is $\dfrac{E}{pr}$, and if $p^2 = \dfrac{c}{l-m}$ we find the actual value is $\dfrac{E\sin\eta}{pr}$ where $\tan\eta = \dfrac{r}{2pm}$. From which it appears that the two

bands in such spectra may be looked on as derived from the vibrations governed by

$$(l+m)\ddot{x} + r\dot{x} + cx = Ee^{\iota pt}, \quad (l-m)\ddot{x} + r\operatorname{cosec}\eta\dot{x} + cx = Ee^{\iota pt}.$$

Of these, the former represents a band on the near side of, and sharper than that of the single vibration centre, while the latter represents a diffuse band in the more remote regions.

The former band will therefore tend to break up into lines.

It must, however, be noticed that if m is small, the bands will probably coalesce to form a single wide band.

We assume that in asymmetrical cases, provided the asymmetry is not too marked, a similar kind of result will be obtained as to the relative sharpness of the bands ; the experimental evidence in favour of this is abundant.

Substances belonging to the above type are fairly numerous : the ketones [3, 13, 19] and ethylene [6] derivatives may be quoted. The two bands demanded by theory are found, but the more remote band is beyond $\lambda 200$.

III. Two *similar* vibration centres with a third the frequency of which is great. The coefficients of induction are as follows :

	x	y	ξ
x	l	m	f
y	m	l	g
ξ	f	g	l_1

It is easy to see that the frequencies are given by

$$\begin{vmatrix} lp^2-c, & mp^2, & fp^2 \\ mp^2, & lp^2-c, & gp^2 \\ fp^2, & gp^2 & l_1p^2-c_1 \end{vmatrix} = 0$$

and c_1 is by supposition large compared with f, g, l_1.
The equation reduces to

$$(c_1-l_1p^2)\{(lp^2-c)^2-m^2p^4\}+p^4\{(f^2+g^2)(lp^2-c)-2fgmp^2\}=0.$$

It is easy to see that if $\dfrac{c_1}{l_1} > \dfrac{c}{l\pm m}$ two values of p^2 are

approximately $\qquad \dfrac{c}{l\pm m}\left(1-\tfrac{1}{2}\dfrac{c}{c_1}\left(\dfrac{f\pm g}{l\pm m}\right)^2\right).$

The bands are therefore *both* shifted towards the visible region by the introduction of the new vibration centre. The effect is also seen to be equivalent to a diminution of c. Therefore, in examining the effect of say a methyl group, we will not look on it as a separate vibration centre, but will diminish the value of c for the atom to which it is attached.

IV. *Four centres placed partly symmetrically.*

x and y correspond, so do ξ and η, so that (x, ξ) is a group of the kind considered above, and (y, η) is an identical group :

e. g.
$$\begin{array}{cc} \overset{\xi}{} & \overset{x}{} \\ H C = O \\ | \quad | \\ H C = O \\ \underset{\eta}{} \quad \underset{y}{} \end{array}$$
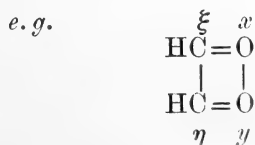
The coefficients used are given in the following table :—

	x	y	ξ	η
x	l	m	f	g
y	m	l	g	f
ξ	f	g	l_1	m_1
η	g	f	m_1	l_1

Proceeding as before, we find that the frequency equation breaks up into the two equations

$$[(l+m)p^2-c]\,[(l_1+m_1)p^2-c_1] = (f+g)^2p^4 \quad . \text{ (viii.)}$$

$$[(l-m)p^2-c]\,[(l_1-m_1)p^2-c_1] = (f-g)^2p^4 \quad . \quad \text{(ix.)}$$

and the characteristic equations reduce to

$$\mathrm{X}\big[\{(l+m)p^2-r\iota p-c\}\{(l_1+m_1)p^2-r_1\iota p-c_1\}-(f+g)^2p^4\big]$$
$$= -\mathrm{E}\big[l_1+m_1)p^2-(f+g)p^2-r_1\iota p-c_1\big] \quad \text{(x.)}$$

and a similar equation for Ξ.

It can be seen that equations (viii.) and (ix.) correspond to equations (v.), and (x.) to (vii.), the difference being in the induction coefficients only. Now (v.) and (vi.) are the equations of the (x, ξ) (or y, η) group independently (allowing for the change of notation).

It appears from the above that the four bands of the system may be looked on as derived from the two bands of either group by displacement. This in the case of the bands given by (viii.) is toward the regions of greater wave-lengths, and the bands produced by the displacement in this direction will tend to be sharpest. The direction of displacement of the bands given by (ix.) depends on the relative values of the various coefficients. It appears, then, that the groups affect one another in the same general way as simple oscillation centres.

Thus, for example, a group which gives two bands A, B (fig. 1) will give rise to four bands, C, D, E, F, when associated with a similar group, and the appearance of the curve will be as in fig. 2.

If m is small, C and E may coalesce to form a single broad band.

We have seen that the band C is likely to be sharp, while F may be very diffuse. This, it is suggested, is the so-called general absorption, which is really part of a diffuse band in the most refrangible regions [3].

The asymmetrical case of the above is undeveloped, but it is fair to assume an interpretation similar to the above, viz., the thrusting apart of the bands due to the constituent groups.
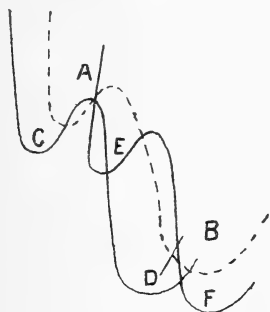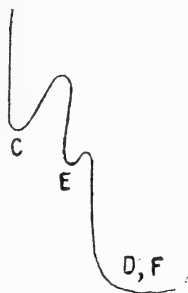
Fig. 1. Fig. 2.

There are many substances of the above type, *e. g.*, diketones [19], diolefines [6], and unsaturated ketones [20], but in no case has the investigation covered the whole region in which bands should occur. The results obtained in the regions examined do, however, correspond accurately with this theory.

The importance of §§ III.–IV. lies in the fact that we cannot in most cases deal with isolated centres in practical work, since even when they can exist their bands are usually outside the ordinary regions. We have therefore to investigate the influence of groups and calculate from them the constants for the free centres. Also, as stated above, even the simple bands in reality are made up of fine lines ; it is of importance to show cause why these should move together. The above reasoning, while by no means conclusive, suggests that this will be the case and no exceptions have been met with in practice.

V. *The Benzene System.*

This consists of six identical vibration centres arranged in accordance with the laws of isomerism, in a ring or otherwise.

The coefficients of induction are :

self-induction l ;

mutual induction between ortho carbons m_o

meta   ,, m_m

para   ,, m_p.

The equations of motion are :

$$l\ddot{x}_1 + m_o\ddot{x}_2 + m_m\ddot{x}_3 + m_p\ddot{x}_4 + m_m\ddot{x}_5 + m_o\ddot{x}_6 + r\dot{x}_1 + cx_1 = \mathrm{E}e^{\iota pt}, \&\mathrm{c}.$$

The frequency equation is

$$\begin{vmatrix} lp^2 - c, & m_o p^2, & m_m p^2, \&\mathrm{c}. \\ m_o p^2, & lp^2 - c, & \\ & & \&\mathrm{c}. \end{vmatrix} = 0 \quad . \quad . \quad \text{(xi.)}$$

and from this the squares of the frequencies are :

$$(\alpha)\ \frac{c}{l + m_p + 2m_o + m_m}, \qquad (\beta)\ \frac{c}{l + m_o - m_m + m_p},$$

$$(\gamma)\ \frac{c}{l + m_p - m_o + m_m}, \qquad (\delta)\ \frac{c}{l - m_p - 2m_o - m_m}.$$

The second and third of these represent coincident roots of the equation. This cannot mean more than the coincidence of two bands, *i. e.* a very deep band.

Since m_o will clearly be greater than m_m or m_p, the above are in order of magnitude.

The four bands will be called the α, β, γ, δ bands respectively.

Characteristic equation.

This degenerates into

$$X[(l + m_p + 2m_o + m_m)p^2 - r\iota p - c] = -\mathrm{E}. \quad . \quad \text{(xii.)}$$

From this we see that the least refrangible band may be derived from the equation

$$(l + mp + 2m_o + m_m)p\ddot{x} + r\dot{x} + cx = \mathrm{E}e^{\iota pt}\ (\alpha)$$

and the others from

$$\mathrm{L}\ddot{x} + r \operatorname{cosec} \eta + cx = \mathrm{E}e^{\iota pt},$$

where

$$\mathrm{L} = (l + m_o - m_m - m_p), \qquad \tan \eta = \frac{r}{p(m_o + 3m_m + 2m_p)} \text{ for } \beta \text{ band.}$$

$$= (l - m_o - m_m + m_p), \qquad\qquad = \frac{r}{p(3m_o + 3m_m)} \qquad ,,\ \gamma\ ,,$$

$$= (l - 2m_o + 2m_m - m_p) \qquad\qquad = \frac{r}{p(4m_o + 2m_p)} \qquad ,,\ \delta\ ,,$$

Since, as has been said, m_o is larger than m_m or m_p, it follows that there is a diminution of the induction coefficient and a reduction of tan η, *i. e.* an *increase* of the friction coefficient in the series. The bands therefore gradually become more diffuse on passing towards the extreme ultraviolet, while the first may be expected to be exceptionally sharp. This it in fact is, for it breaks up even in solution, giving the seven well-known benzene bands described by Hartley, 4, 5, 11 [*].

Only the α [4] and β [7] series of bands have been actually observed ; the constants have been calculated from these, and it was then found that the γ and δ series are out of range of all the present spectroscopes.

Non-symmetrical ring systems (toluene, pyridine, &c.).— The complete investigation of these cases need not be given. They are, in general, too complex for treatment, but in any particular case can be worked out numerically when the requisite data are available. It appears that the bands will be of the same general character as the benzene system, but the double bands β and γ will separate into their components [†]. These, however, will probably not be sufficiently far apart to be distinct, so the total effect will be a single broad band.

Also the band corresponding to α will become less sharp as the departure from symmetry becomes more and more pronounced.

VI. *A benzene nucleus* with an independent oscillation centre outside it.

We must assume that the coefficients of the benzene system are unaltered by the presence of the new centre.

The coefficients for this are denoted by λ, ϖ, μ_o, μ_m, μ_p.

This case also is too complex for general treatment. No reasons can be given for assuming that the benzene group in general acts like the single centre of § II. or the simple group of § IV.

[*] It may be stated as a general principle that the " nearest " band is the one most likely to break up into small bands, and this is most likely to happen when the frequency and characteristic equation break up into factors.

In addition, the substance in question must be fairly volatile, since bands always tend to coalesce as the temperature increases.

[†] In the monosubstituted derivatives, and in pyridine, it appears that one component each of the β and γ bands is altogether unchanged. A similar result is obtained when an independent oscillation centre is introduced into the molecule, and also in the case of quinone, diphenyl, diphenylmethane, &c.

If, however, the new centre is such and so situated that ϖ is small, μ_o, μ_m, μ_p negligible, the frequency equation reduces to

$$(c_1 - l_1 p^2)\Delta - \varpi^2 p^2 \Delta' = 0, \quad . \quad . \quad . \quad \text{(xiii.)}$$

where, introducing the numerical values of the constants,

$$\Delta = (1 - 6\cdot25p^2)(1 - 4\cdot17p^2)^2(1 - 2\cdot59p^2)^2(1 - 1\cdot89p^2),$$

$$\Delta' = 3\cdot60p^2(1 - 5\cdot14p^2)(1 - 3\cdot14p^2)(1 - 3\cdot00p^2)(1 - 4\cdot17p^2)(1 - 2\cdot59p^2).$$

Hence the β and γ bands should appear and

(A) If the new centre is on the near side of $p^2 = \dfrac{1}{5\cdot14}$, *i.e.* $\lambda\,227$, two bands will be seen in the normal region (*e.g.* anilines [4, 11, 22]).

(B) If it is on the far side of $\lambda\,227$, only one band (*e.g.* phenols [9, 10]).

We can also work out the cases of two centres attached to one ring in the same way. The para case is the only one which factorizes, and hence we expect (p. 201 note) para derivatives to show narrow bands more readily than the ortho and meta. This is found correct.

VII. A " group" attached to a benzene ring, *e.g.* $C_6H_5 . CHO$, benzaldehyde.

If ϖ and ψ are the inductions between the atoms of the group and the carbon to which they are attached, and the approximation holds, the equation is

$$\Delta\{(l_1 p^2 - c_1)(l_2 p^2 - c) - m_{12}^2 p^4\} + \Delta' p^2\{\varpi^2(l_2 p^2 - c_2)$$
$$+ \psi^2(l_1 p^2 - c_1) - 2\varpi\psi m_{12}p^2\} = 0 . \quad \text{(xiv.)}$$

There will be two bands on the near side of $\lambda\,227$ and sometimes a third very near $\lambda\,227$, *e.g.* benzaldehyde [21], styrol, methylazobenzene [25].

VIII. Two *similar* groups each united to a ring, $C_6H_5N = N - C_6H_5$.

If θ is the mutual coefficient of the two nearest carbons of the rings, the frequency equation breaks up into

$$\{c_1 - (l_1 \pm m)p^2\}(\Delta \pm \theta\Delta') = +p^2(\varpi \pm \psi)^2\Delta' . . \quad \text{(xv.)}$$

It follows that if the group between the phenyls gives rise to a band on the near side of $\lambda 250$, at least two bands appear, otherwise only one, *e. g.* azobenzene [25], hydrazobenzene [18], and stilbene.

IX. Two rings united by one or more methylene groups (the effect is apparently just felt through two).

The frequency equation is

$$\Delta \pm \theta \Delta' = 0, \quad \ldots \ldots \ldots \text{(xvi.)}$$

e. g. diphenyl methane [18], dibenzyl.

When the rings are united directly, as in diphenyl, the approximation required for the above does not hold. It will be noticed that the β and γ bands will be found in the above cases (VI.), (VII.), (VIII.), and (IX.).

It is easy to see that (xv.) is related to (xvi.) in the same way as (xiii.) to the benzene equation, $\Delta = 0$ (xi.).

The following values of the constants may be quoted as giving numerical results agreeing closely with the observed values :—

Values of c.

Carbon, $-\dot{C}H_2$ ·297, $-\dot{C}HMe$ ·278, $-\dot{C}Me_2$ ·252.
$-\dot{C}MeEt$ ·247, $-\dot{C}Et_2$ ·241.

Oxygen, hydroxylic, ·60.
    ketonic, ·20.

[In the lower aldehydes the stability constant is much smaller, as can be seen from the position of the bands. This is especially marked in formaldehyde, and is in accord with the chemical nature of these substances.]

Nitrogen, $-NH_2$ ·17 (assuming $l=1$, *i. e.* 1 electron free).
    $-\dot{N}Me_2$ ·15.
    $=\dot{N}$ ·12 in azo derivatives.
Iodine,   I ·16.

Values of m.

$\dot{C}$ to C, ·13 if adjacent.
    ·02 if separated by one carbon atom.
$\dot{C}$ to $\dot{O}$ in ketones, ·48.
$\dot{C}$ to OH (in benzene derivatives), 1·49 (?).
$\dot{C}$ to $=\dot{N}$ azo ,,   ,,   ·57 if adjacent.
            ·07 if separated by one
$-\dot{C}$ to N (amido), ·543.   atom.
$=\dot{N}$ to $=\dot{N}$, ·38.
  (in azo derivatives),
I to I att. to same carbon, ·38.
 to adjacent carbons,   ·04.
In benzene m_o = ·275 ⎫ assuming m_m and m_p almost equal.
   m_m = ·064 ⎬ There are only two equations to
   m_p = ·056 ⎭ calculate the three unknowns.

The value of m is increased in ratio $1 : 1\cdot6$ if the atoms are between two unsaturated carbons or if they are between two phenyl groups.

Using the above figures satisfactory results are obtained, the difference between calculated and observed positions of the bands being small except in very complex substances. In these cases, however, the *numbers* and approximate positions of the bands calculated and observed are in agreement.

In conclusion the author wishes to thank Prof. Sir J. J. Thomson for his interest in this paper, and Mr. G. Birtwistle for much valuable advice and criticism.

August, 1914.

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APPENDIX.—I am indebted for the following proof of the existence of the mutual induction term to Mr. Birtwistle, of Pembroke College.

The field due to a system of electrons moving in small closed orbits about mean points $x_1y_1z_1$, $x_2y_2z_2$, &c. has been expressed (so far as the part affecting radiation is concerned)

by Prof. H. M. Macdonald ('Electric Waves,' p. 176) in the form

$$X = -\frac{\partial^2}{\partial t^2} \Sigma \frac{e_1 \xi_1{}'}{r_1} - c^2 \frac{\partial \psi'}{\partial x}, \&c. \qquad (A)$$

$$\alpha = \frac{\partial^2}{\partial y \partial t} \Sigma \frac{e_1 \zeta_1{}'}{r_1} - \frac{\partial^2}{\partial z \partial t} \Sigma \frac{e_1 \eta_1{}'}{r_1}, \&c. \quad (B)$$

where r_1 is the distance of the field point xyz from $x_1 y_1 z_1$,

$\xi_1 \eta_1 \zeta_1$, the position of electron 1 at time t,

$\xi_1{}' \eta_1{}' \zeta_1{}'$, ,, ,, $-\dfrac{r_1}{c}$,

c being the velocity of light,

and $\qquad \psi' = \dfrac{\partial}{\partial x} \Sigma \dfrac{e_1 \xi_1{}'}{r_1} + \dfrac{\partial}{\partial y} \cdots + \dfrac{\partial}{\partial z} \cdots$

the summation being taken for all the electrons.

The electrokinetic energy is

$$\frac{1}{2} \iiint (F \dot{f} + +) d\tau,$$

where

$$\alpha = \frac{\partial H}{\partial y} - \frac{\partial G}{\partial z}, \&c. \quad (C), \quad \text{and } 4\pi c^2 f = X \quad (D);$$

and since from (B) and (C)

$$F = \frac{\partial}{\partial t} \cdot \Sigma \frac{e_1 \xi_1{}'}{r_1}$$

the energy is, using (A) and (D),

$$\frac{1}{8\pi c^2} \iiint \left[\frac{\partial}{\partial t} \Sigma \frac{e_1 \xi_1{}'}{r_1} \frac{\partial}{\partial t} \left\{ -\frac{\partial^2}{\partial t^2} \Sigma \frac{e_1 \xi_1{}'}{r_1} - c^2 \frac{\partial \psi'}{\partial x} \right\} + (\eta) + (\zeta) \right] d\tau,$$

the integral being taken through all space.

If the velocities are small enough compared with c, the expression for the energy reduces to the following (the dashes being now omitted):

$$-\frac{1}{8\pi} \iiint \left[\frac{\partial}{\partial t} \Sigma \frac{e_1 \xi_1}{r_1} \frac{\partial}{\partial t} \frac{\partial \psi}{\partial x} + \cdots \right] d\tau,$$

or to

$$-\frac{1}{8\pi}\iiint\left[\Sigma\frac{e_1\dot{\xi}_1}{r_1}\left\{\Sigma e_1\dot{\xi}_1\frac{\partial^2}{\partial x^2}\left(\frac{1}{r_1}\right)+\Sigma e_1\dot{\eta}_1\frac{\partial^2}{\partial x\partial y}\left(\frac{1}{r_1}\right)+\ \dots\right\}+\ \dots\right]d\tau,$$

which is of the form

$$\mathrm{L}_1 e_1{}^2\dot{\xi}_1{}^2+\ \dots\qquad+\mathrm{M}_{12}e_1 e_2\dot{\xi}_1\dot{\xi}_2+\ \dots$$

the coefficients L_1, M_{12}, &c. being independent of t.

This justifies the introduction of "mutual induction" terms into the equations of motion, and the analogy to currents.

If c is not much larger than the velocities, then L_1, M_{12}, &c. are not truly constant.

XXII. *Notices respecting New Books.*

The Call of the Stars: *a popular introduction to a knowledge of the Starry Skies.* By JOHN R. KIPPAX, M.D., LL.B., Author of Comets and Meteors, Churchyard Literature, &c. 418+xviii pp., 9 in.×$5\frac{1}{2}$ in. 54 illustrations. G. P. Putnam's Sons, New York and London: Knickerbocker Press. 10s. 6d. net.

THE author aims at "a concise and accurate story of the starry heavens, together with the legendary lore that time and fancy have associated with them." The backward gaze indicated in the second object prepares us to find that the most modern work receives very little attention: for instance, the studies of stellar movement, which have engrossed so much attention of late, are dismissed with a few words in the opening chapter; and very little is said about modern solar research. Since the author has collected his information chiefly from other text-books, this feature might perhaps be ascribed to the fact that he must necessarily be behind them in date; but it is a pity that he did not consult, for instance, Darwin's "Tides," which has been a classic for many years now. Apart from this defect, the book is a well-written and interesting account of the main facts; and it can do no possible harm to be reminded, alongside the modern account of Saturn, of the mythology and worship of the associated deity in times past. The illustrations are excellent; and there is a good collection of poetic references. There are a few slips, as when the "isothermal layer" of our atmosphere is called a "reversing layer" p. 312; but on the whole the information is remarkably accurate and sound; and the index has been made with care.

XXIII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. xxviii. p. 842.]

November 18th, 1914.—Dr. A. Smith Woodward, F.R.S., President, in the Chair.

THE following communications were read :—

1. 'On a Raised Beach on the Southern Coast of Jersey.' By Andrew Dunlop, M.D., F.G.S.

Last June Mr. E. F. Guiton drew attention to a raised beach recently exposed on the southern coast of the island. It is on the eastern slope of the ridge between Le Hocq and Pontac, and the section, facing northwards, shows the following succession of beds from above downwards :—

		Thickness in feet	inches.
(1)	Earthy loam, with a layer of rubble	4	0
(2)	Stiff brownish-red clay	1	0
(3)	Yellow loamy clay, containing waterworn pebbles and angular fragments..	3	4
(4)	Coarse brown sand	3	6
(5)	Waterworn pebbles, closely packed in a matrix of coarse brown sand...	4	6

The rock beneath is fine red granite. The section is terminated at its western end by sloping rock, and there, between the rock and the lower beds, is a layer of stiff brownish-yellow clay about 2 feet thick, which is continued for a short distance under the bed of pebbles.

The base of the section is about 50 feet above mean sea-level.

The pebbles in both the upper and the lower beds are mostly of the fine red granite of the locality, but there are some of diabase and of quartzite, as well as a few of flint. Flint is, of course, foreign to the island, but there are many flint-pebbles on the recent beaches, especially on the north-eastern coast. Flint pebbles have also been found in at least two low-level raised beaches, and flint-pebbles and fragments have been noticed in the yellow clay. Pebbles and fragments of Devonian shale have also been found in what appears to be a remaining fragment of a raised beach on the south-western coast.

Col. Warton recently pointed out a raised beach, not previously noticed, in the railway-cutting near the Eastern Railway-station. This is also on the south side of the island, not far from the coast. Its base is about 55 feet above mean sea-level, and it is covered by a thick bed of yellow loamy clay.

2. 'On Tachylyte Veins and Assimilation Phenomena in the Granite of Parijs (Orange Free State).' By Prof. S. James Shand, D.Sc., Ph.D., F.G.S.

The district described is the neighbourhood of Parijs Township, which is situated on the Vaal River and lies upon the northern portion of the Vredefort granite-mass.

The so-called 'granite' near Parijs is a red and grey streaky gneiss.

often traversed, both parallel to and across the foliation, by veins of red pegmatite : these are of a later period of consolidation than the rest of the rock. The author concludes, from field-evidence, that the grey facies of the gneiss results from assimilation of the country-rock by an ascending magma ; while the red facies represents the residual portion of the same magma.

The special interest of the district, however, lies not so much in the granite, as in a system of tachylytic veins which everywhere intersects the granitic rocks. These veins range from a fraction of an inch to 2 feet in thickness, but in the thicker veins there are numerous inclusions of the country-rock. They are irregular in form, thickness, and direction, and are due to the intrusion of a basic magma which underlay the district. The author describes the microscopic characters of these tachylytes, and comments on their general glassy and cryptocrystalline nature, which he does not regard as a result of chilling, but suspects is dependent upon the viscosity of the basic magma.

He brings forward evidence to prove that the position occupied by the tachylyte is independent of tectonic features, but follows directly from solution and corrosion of the granitic rocks by the basic magma.

XXIV. *Intelligence and Miscellaneous Articles.*

### PRESSURE OF RADIATION ON A RECEDING REFLECTOR : CORRIGENDA. BY SIR J. LARMOR.

THE correct statement (Phil. Mag. Nov. 1914, pp. 706–707) is that the æthereal momentum inside and the mechanical forces sustained by the bodies inside are the result of the stress transmitted across the boundary : the sign of the extra tangential traction must therefore be changed.

Also equation (A) makes θ' of opposite sign to θ : to adapt it to (B) the sign of its first term must thus be changed.

Equation (B) means that for oblique total reflexion, as for direct, the force intensity is altered in amplitude inversely as the wave-length, and in no other respect. Thus the phenomena can still be formulated under a simple scheme which expresses that the radiation carries momentum with it, and on total reflexion the amplitude of the fundamental displacement in the æther is conserved[*]. Then perhaps the validity may be asserted beyond the first power of v/a : but for an ordinary partial reflector, the propagation is in part into matter whose molecular structure is naturally too complex for such a scheme.

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[*] I observe now that in a clear and concise investigation in the Phil. Mag. for December, conducted in terms of momentum alone in Prof. Poynting's manner, and thus applicable only to propagation in free space, Mr. T. Harris finds that the resultant thrust on the perfect receding reflector is along the normal. This fact either may be regarded as a simple geometrical consequence of the principle above stated, or else may be formulated as an alternative principle.

Fig. 6.
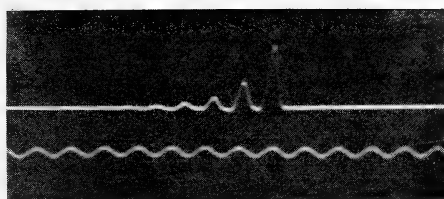
Primary current 1·5 amperes.

Fig. 7.
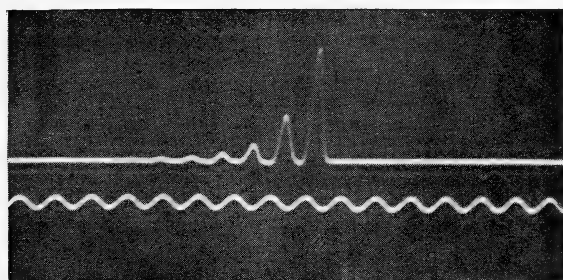
Primary current 2 amperes.

Fig. 8.

Two successive breaks by motor interruptor.

Fig. 1.

Fig. 3.

Fig. 5.

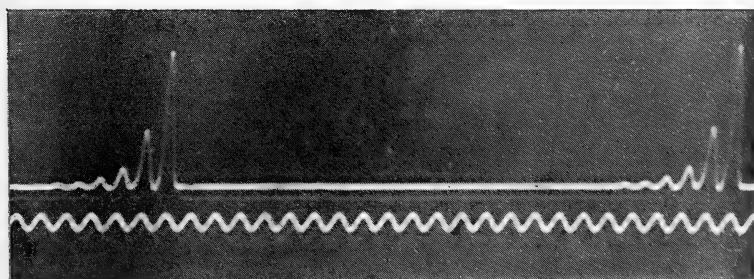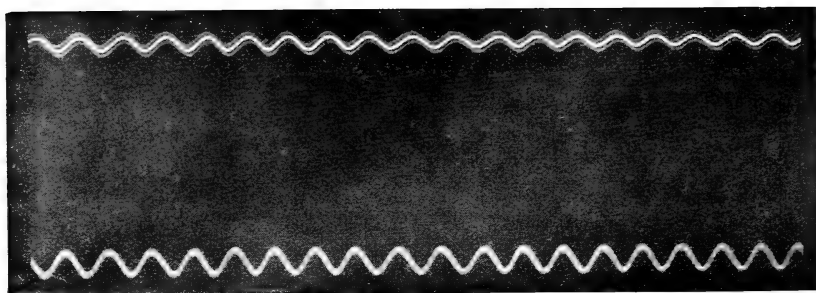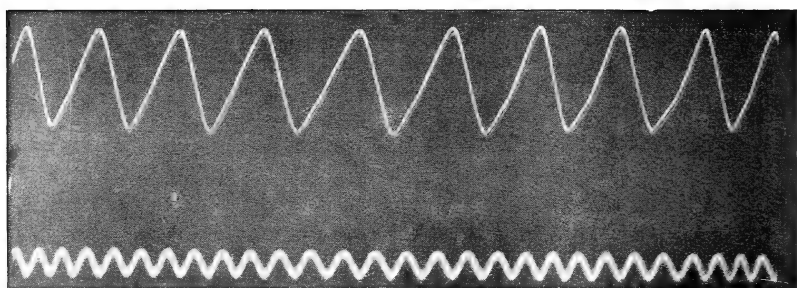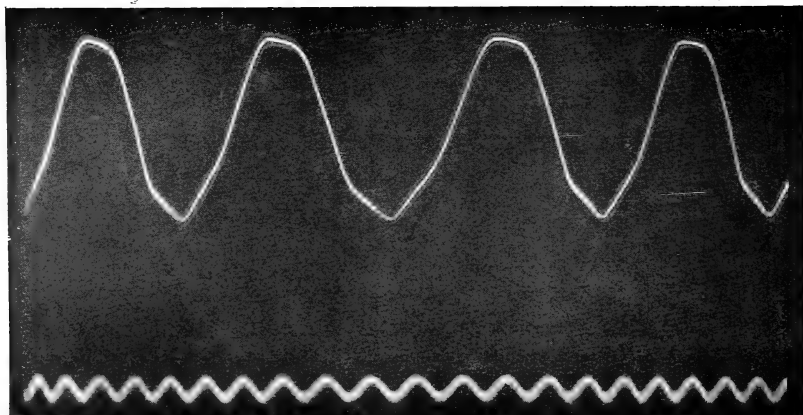Fig. 2.
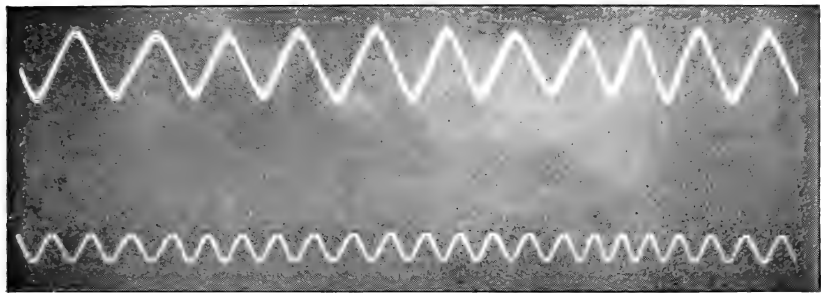
Fig. 4.
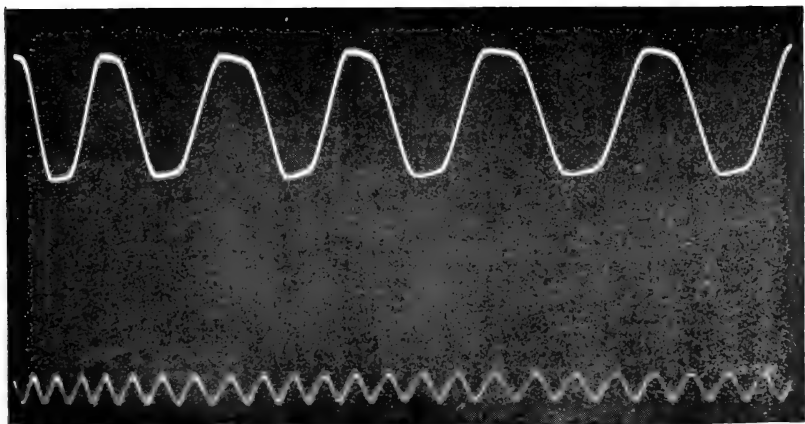
Fig. 6.
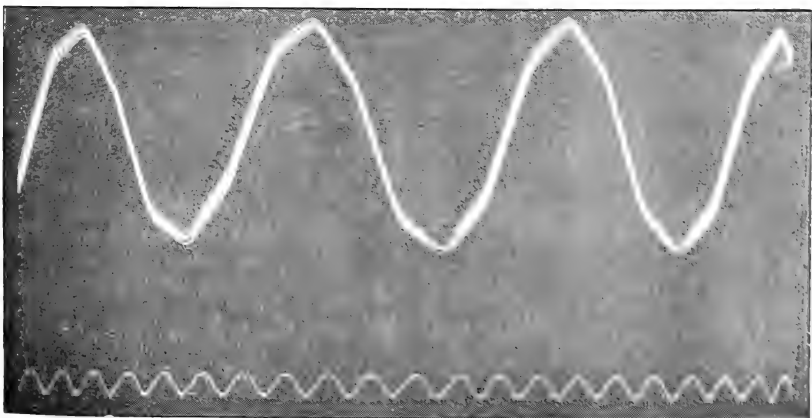
z
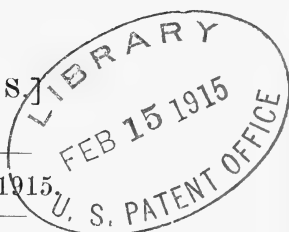
XXV. *Some Problems concerning the Mutual Influence of Resonators exposed to Primary Plane Waves.* By Lord RAYLEIGH, *O.M., F.R.S.*[*]

RECENT investigations, especially the beautiful work of Wood on " Radiation of Gas Molecules excited by Light " [†], have raised questions as to the behaviour of a cloud of resonators under the influence of plane waves of their own period. Such questions are indeed of fundamental importance. Until they are answered we can hardly approach the consideration of *absorption*, viz. the conversion of radiant into thermal energy. The first action is upon the molecule. We may ask whether this can involve on the average an increase of translatory energy. It does not seem likely. If not, the transformation into thermal energy must await collisions.

The difficulties in the way of answering the questions which naturally arise are formidable. In the first place we do not understand what kind of vibration is assumed by the molecule. But it seems desirable that a beginning should be made ; and for this purpose I here consider the case of the simple aerial resonator vibrating symmetrically. The results cannot be regarded as even roughly applicable in a quantitative sense to radiation, inasmuch as this type is

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[*] Communicated by the Author.

[†] A convenient summary of many of the more important results is given in the Guthrie Lecture, Proc. Phys. Soc. vol. xxvi. p. 185 (1914).

inadmissible for transverse vibrations. Nevertheless they may afford suggestions.

The action of a simple resonator under the influence of suitably tuned primary aerial waves was considered in 'Theory of Sound,' § 319 (1878). The primary waves were supposed to issue from a simple source at a finite distance c from the resonator. With suppression of the time-factor, and at a distance r from their source, they are represented [*] by the potential

$$\phi = \frac{e^{-ikr}}{r}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which $k = 2\pi/\lambda$, and λ is the wave-length ; and it appeared that the potential of the secondary waves diverging from the resonator is

$$\psi = \frac{e^{-ikc}}{ikc} \frac{e^{-ikr'}}{r'}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

so that

$$4\pi r'^2 \operatorname{Mod}^2 \psi = 4\pi/k^2 c^2. \quad . \quad . \quad . \quad . \quad (3)$$

The left-hand member of (3) may be considered to represent the energy dispersed. At the distance of the resonator

$$\operatorname{Mod}^2 \phi = 1/c^2.$$

If we inquire what area S of primary wave-front propagates the same energy as is dispersed by the resonator, we have

$$S/c^2 = 4\pi/k^2 c^2,$$

or $\qquad\qquad S = 4\pi/k^2 = \lambda^2/\pi. \quad . \quad . \quad . \quad . \quad (4)$

Equation (4) applies of course to *plane* primary waves, and is then a particular case of a more general theorem established by Lamb [†].

It will be convenient for our present purpose to start *de novo* with plane primary waves, still supposing that the resonator is simple, so that we are concerned only with symmetrical terms, of zero order in spherical harmonics.

Taking the place of the resonator as origin and the direction of propagation as initial line, we may represent the primary potential by

$$\phi = e^{ikr\cos\theta} = 1 + ikr\cos\theta - \tfrac{1}{2}k^2 r^2 \cos^2\theta + \ldots \quad . \quad (5)$$

[*] A slight change of notation is introduced.

[†] Camb. Trans. vol. xviii. p. 348 (1899) ; Proc. Math. Soc. vol. xxxii. p. 11 (1900). The resonator is no longer limited to be *simple*. See also Rayleigh, Phil. Mag. vol. iii. p. 97 (1902) ; Scientific Papers, vol. v. p. 8.

The potential of the symmetrical waves issuing from the resonator may be taken to be

$$\psi = \frac{ae^{-ikr}}{r} = \frac{a}{r}(1-ikr+\ldots). \quad \quad (6)$$

Since the resonator is supposed to be an ideal resonator, concentrated in a point, r is to be treated as infinitesimal in considering the conditions to be there satisfied. The first of these is that no *work* shall be done at the resonator, and it requires that total pressure and total radial velocity shall be in quadrature. The total pressure is proportional to $d(\phi+\psi)/dt$, or to $i(\phi+\psi)$, and the total radial velocity is $d(\phi+\psi)/dr$. Thus $(\phi+\psi)$ and $d(\phi+\psi)/dr$ must be in the same (or opposite) phases, in other words their *ratio* must be *real*. Now, with sufficient approximation,

$$\phi+\psi=1+\frac{a}{r}(1-ikr), \quad \frac{d(\phi+\psi)}{dr}=-\frac{a}{r^2};$$

so that

$$\frac{1}{a}-ik = \text{real.} \quad \quad (7)$$

If we write

$$a=Ae^{ia}, \quad 1/a=A^{-1}e^{-ia}, \quad \quad (8)$$

then

$$A=-k^{-1}\sin\alpha. \quad \quad (9)$$

So far α is arbitrary, since we have used no other condition than that no work is being done at the resonator. For instance, (9) applies when the source of disturbance is merely the presence at the origin of a small quantity of gas of varied character. The peculiar action of a *resonator* is to make A a maximum, so that $\sin\alpha=\pm1$, say -1. Then

$$A=1/k, \quad a=-i/k, \quad \quad (10)$$

and

$$\psi=-\frac{ie^{-ikr}}{kr}. \quad \quad (11)$$

As in (3),

$$4\pi r^2 \text{Mod}^2\psi = 4\pi/k^2 = \lambda^2/\pi, \quad \quad (12)$$

and the whole energy dispersed corresponds to an area of primary wave-front equal to λ^2/π.

The condition of resonance implies a definite relation between $(\phi+\psi)$ and $d(\phi+\psi)/dr$. If we introduce the

value of a from (10), we see that this is

$$\frac{\phi+\psi}{d(\phi+\psi)/dr} = \frac{1/a+1/r-ik}{-1/r^2} = -r \; ; \quad . \quad . \quad (13)$$

and this is the relation which must hold at a resonator so tuned as to respond to the primary waves, when isolated from all other influences.

The above calculation relates to the case of a single resonator. For many purposes, especially in Optics, it would be desirable to understand the operation of a company of resonators. A strict investigation of this question requires us to consider each resonator as under the influence, not only of the primary waves, but also of the secondary waves dispersed by its neighbours, and in this many difficulties are encountered. If, however, the resonators are not too near one another, or too numerous, they may be supposed to act independently. From (11) it will be seen that the standard of distance is the wave-length.

The action of a number (n) of similar and irregularly situated centres of secondary disturbance has been considered in various papers on the light from the sky [*]. The phase of the disturbance from a single centre as it reaches a distant point, depends of course upon this distance and upon the situation of the centre along the primary rays. If all the circumstances are accurately prescribed, we can calculate the aggregate effect at a distant point, and the resultant intensity may be anything between 0 and that corresponding to complete agreement of phase among all the components. But such a calculation would have little significance for our present purpose. Owing to various departures from ideal simplicity, *e. g.* want of homogeneity in the primary vibrations, movement of the disturbing centres, the impossibility of observing what takes place at a mathematical point, we are in effect only concerned with the average, and the average intensity is n times that due to a single centre.

In the application to a cloud of acoustic resonators the restriction was necessary that the resonators must not be close compared with λ ; otherwise they would react upon one another too much. This restriction may appear to exclude the case of the light from the sky, regarded as due mainly to the molecules of air ; but these molecules are not resonators—at any rate as regards visible radiations. We can most easily argue about an otherwise uniform medium

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[*] Compare also "Wave Theory of Light," Enc. Brit. xxiv. (1888), § 4 ; Scientific Papers, vol. iii. pp. 53, 54,

disturbed by numerous small obstacles composed of a medium of different quality. There is then no difficulty in supposing the obstacles so small that their mutual reaction may be neglected, even although the average distance of immediate neighbours is much less than a wave-length. When the obstacles are small enough, the whole energy dispersed may be trifling, but it is well to observe that there must be some. No medium can be fully transparent in all directions to plane waves which is not itself quite uniform. Partial exceptions may occur, *e. g.* when the want of uniformity is a stratification in plane strata. The dispersal then becomes a regular reflexion, and this may vanish in certain cases, even though the changes of quality are sudden (black in Newton's rings) *. But such transparency is limited to certain directions of propagation.

To return to resonators: when they may be close together, we have to consider their mutual reaction. For simplicity we will suppose that they all lie on the same primary wave-front, so that as before in the neighbourhood of each resonator we may take

$$\phi = 1, \quad d\phi/dr = 0. \quad . \quad . \quad . \quad (14)$$

Further, we suppose that all the resonators are similarly situated as regards their neighbours, *e. g.*, that they lie at the angular points of a regular polygon. The waves diverging from each have then the same expression, and altogether

$$\psi = a \left\{ \frac{e^{-ikr_1}}{r_1} + \frac{e^{-ikr_2}}{r_2} + \ldots \right\}, \quad . \quad . \quad (15)$$

where $r_1, r_2, \ldots$ are the distances of the point where ψ is measured from the various resonators, and a is a coefficient to be determined. The whole potential is $\phi + \psi$, and it suffices to consider the state of things at the first resonator. With sufficient approximation

$$\phi + \psi = 1 + \frac{a}{r_1}(1 - ikr_1) + a \Sigma \frac{e^{-ik\mathrm{R}}}{\mathrm{R}} \ldots, \quad . \quad . \quad (16)$$

R being the distance of any other resonator from the first, while (as before)

$$\frac{d(\phi + \psi)}{dr} = -\frac{a}{r_1^2}. \quad . \quad . \quad . \quad . \quad (17)$$

We have now to distinguish two cases. In the first, which is the more important, the tuning of the resonators is

* See Proc. Roy. Soc. vol. 86 A, p. 207 (1912).

such that each singly would respond as much as possible to the primary waves. The ratio of (16) to (17) must then, as we have seen, be equal to $-r_1$, when r_1 is indefinitely diminished. Accordingly

$$\frac{1}{a} = ik - \Sigma \frac{e^{-ik\mathrm{R}}}{\mathrm{R}}, \quad \cdots \quad \cdots \quad (18)$$

which, of course, includes (10). If we write $a = \mathrm{A}e^{i\alpha}$, then

$$\mathrm{A}^2 = \frac{1/k^2}{\left[\Sigma \dfrac{\cos k\mathrm{R}}{k\mathrm{R}}\right]^2 + \left[1 + \Sigma \dfrac{\sin k\mathrm{R}}{k\mathrm{R}}\right]^2}. \quad \cdots \quad (19)$$

The other case arises when the resonators are so tuned that the *aggregate* responds as much as possible to the primary waves. We may then proceed as in the investigation for a single resonator. In order that no work may be done at the disturbing centres, $(\phi + \psi)$ and $d(\phi + \psi)/dr$ must be in the same phase, and this requires that

$$\frac{1}{a} + \frac{1}{r_1} - ik + \Sigma \frac{e^{-ik\mathrm{R}}}{\mathrm{R}} = \text{real},$$

or

$$\frac{1}{a} = \text{real} + ik + i\Sigma \frac{\sin k\mathrm{R}}{\mathrm{R}}. \quad \cdots \quad (20)$$

The condition of maximum resonance is that the real part in (20) shall vanish, so that

$$\frac{1}{a} = ik \left\{ 1 + \Sigma \frac{\sin k\mathrm{R}}{k\mathrm{R}} \right\} \quad \cdots \quad (21)$$

or

$$\mathrm{A} = \frac{1/k}{1 + \Sigma \dfrac{\sin k\mathrm{R}}{k\mathrm{R}}}. \quad \cdots \quad (22)$$

The present value of A^2 is greater than that in (19), as was of course to be expected. In either case the disturbance is given by (15) with the value of a determined by (18), or (21).

The simplest example is when there are only two resonators and the sign of summation may be omitted in (18). In order to reckon the energy dispersed, we may proceed by either of two methods. In the first we consider the value of ψ and its modulus at a great distance r from the resonators. It is evident that ψ is symmetrical with

respect to the line R joining the resonators, and if θ be the angle between r and R, $r_1 - r_2 = \mathrm{R} \cos \theta$. Thus

$$r^2 . \operatorname{Mod}^2 \psi = \mathrm{A}^2 \{2 + 2 \cos (k\mathrm{R} \cos \theta)\} ;$$

and on integration over angular space,

$$2\pi r^2 \int_0^\pi \operatorname{Mod}^2 \psi . \sin \theta \, d\theta = 8\pi \mathrm{A}^2 \left\{ 1 + \frac{\sin k\mathrm{R}}{k\mathrm{R}} \right\}. \quad (23)$$

Introducing the value of A^2 from (19), we have finally

$$2\pi r^2 \int_0^\pi \operatorname{Mod}^2 \psi . \sin \theta \, d\theta = \frac{8\pi k^{-2} \left(1 + \dfrac{\sin k\mathrm{R}}{k\mathrm{R}} \right)}{1 + \dfrac{1}{k^2\mathrm{R}^2} + 2 \dfrac{\sin k\mathrm{R}}{k\mathrm{R}}} . \quad (24)$$

If we suppose that $k\mathrm{R}$ is large, but still so that R is small compared with r, (24) reduces to $8\pi k^{-2}$ or $2\lambda^2/\pi$. The energy dispersed is then the double of that which would be dispersed by each resonator acting alone ; otherwise the mutual reaction complicates the expression.

The greatest interference naturally occurs when $k\mathrm{R}$ is small. (24) then becomes $2k^2\mathrm{R}^2 . 2\lambda^2/\pi$, or $16\pi\mathrm{R}^2$, in agreement with 'Theory of Sound,' § 321. The whole energy dispersed is then much *less* than if there were only one resonator.

It is of interest to trace the influence of distance more closely. If we put $k\mathrm{R} = 2\pi m$, so that $\mathrm{R} = m\lambda$, we may write (24)

$$\mathrm{S} = \frac{2\lambda^2}{\pi} . \mathrm{F}, \quad . \quad . \quad . \quad . \quad . \quad (25)$$

where S is the area of primary wave-front which carries the same energy as is dispersed by the two resonators and

$$\mathrm{F} = \frac{2\pi m + \sin (2\pi m)}{2\pi m + (2\pi m)^{-1} + 2 \sin (2\pi m)}. \quad . \quad . \quad (26)$$

If $2m$ is an integer, the sine vanishes and

$$\mathrm{F} = \frac{1}{1 + (2\pi m)^{-2}}, \quad . \quad . \quad . \quad . \quad . \quad (27)$$

not differing much from unity even when $2m = 1$; and whenever $2m$ is great, F approaches unity.

The following table gives the values of F for values of $2m$ not greater than 2 :—

$2m$.	F.	$2m$.	F.	$2m$.	F.
0·05	0·0459	0·70	0·7042	1·40	1·266
0·10	0·1514	0·80	0·7588	1·50	1·269
0 20	0·3582	0·90	0·8256	1·60	1·226
0·30	0·4836	1·00	0·9080	1·70	1·159
0·40	0·5583	1·10	1·006	1·80	1·088
0·50	0·6110	1·20	1·113	1·90	1·026
0·60	0·6569	1·30	1·208	2·00	0·975

In the case of two resonators the integration in (23) presents no difficulty ; but when there are a larger number, it is preferable to calculate the emission of energy in the dispersed waves from the work which would have to be done to generate them at the resonators (in the absence of primary waves)—a method which entails no integration. We continue to suppose that all the resonators are similarly situated, so that it suffices to consider the work done at one of them—say the first.   From (15)

$$\psi = a \left\{ \frac{1 - ikr}{r} + \Sigma \frac{e^{-ik\mathrm{R}}}{\mathrm{R}} \right\}, \qquad \frac{d\psi}{dr} = -\frac{a}{r^2}.$$

The pressure is proportional to $i\psi$, and the part of it which is in the same phase as $d\psi/dr$ is proportional to

$$a \left\{ k + \Sigma \frac{\sin k\mathrm{R}}{\mathrm{R}} \right\}.$$

Accordingly the work done at each source is proportional to

$$\mathrm{A}^2 \left\{ 1 + \Sigma \frac{\sin k\mathrm{R}}{k\mathrm{R}} \right\}. \quad . \quad . \quad . \quad . \quad . \quad (28)$$

Hence altogether by (19) the energy dispersed by n resonators is that carried by an area S of primary wave-front, where

$$\mathrm{S} = \frac{n\lambda^2}{\pi} \frac{1 + \Sigma \dfrac{\sin k\mathrm{R}}{k\mathrm{R}}}{\left[\Sigma \dfrac{\cos k\mathrm{R}}{k\mathrm{R}} \right]^2 + \left[1 + \Sigma \dfrac{\sin k\mathrm{R}}{k\mathrm{R}} \right]^2}; \quad . \quad . \quad (29)$$

the constant factor being determined most simply by a

comparison with the case of a single resonator, for which $n=1$ and the Σ's vanish. We fall back on (24) by merely putting $n=2$, and dropping the signs of summation, as there is then only one R.

If the tuning is such as to make the effect of the *aggregate* of resonators a maximum, the cosines in (29) are to be dropped, and we have

$$S = \frac{n\lambda^2}{\pi} \frac{1}{1 + \Sigma \frac{\sin k\mathrm{R}}{k\mathrm{R}}} . \quad . \quad . \quad . \quad (30)$$

As an example of (29), we may take 4 resonators at the angular points of a square whose side is b. There are then 3 R's to be included in the summation, of which two are equal to b and one to $b\sqrt{2}$, so that (28) becomes

$$A^2 \left\{ 1 + 2\frac{\sin kb}{kb} + \frac{\sin (kb\sqrt{2})}{kb\sqrt{2}} \right\} . \quad . \quad . \quad (31)$$

A similar result may be arrived at from the value of ψ at an infinite distance, by use of the definite integral *

$$\int_0^{\frac{1}{2}\pi} \mathrm{J}_0(x \sin \theta) \sin \theta \, d\theta = \frac{\sin x}{x} . \quad . \quad . \quad . \quad (32)$$

As an example where the company of resonators extends to infinity, we may suppose that there is a row of them, equally spaced at distance R. By (18)

$$\frac{1}{a} = ik - 2 \left\{ \frac{e^{-ik\mathrm{R}}}{\mathrm{R}} + \frac{e^{-2ik\mathrm{R}}}{2\mathrm{R}} + \frac{e^{-3ik\mathrm{R}}}{3\mathrm{R}} + \dots \right\} . \quad . \quad (33)$$

The series may be summed. If we write

$$\Sigma = e^{-ix} + \frac{h e^{-2ix}}{2} + \frac{h^2 e^{-3ix}}{3} + \dots, \quad . \quad . \quad . \quad (34)$$

where h is real and less than unity, we have

$$\frac{d\Sigma}{dx} = -\frac{i e^{-ix}}{1 - h e^{-ix}},$$

and

$$\Sigma = -\frac{1}{h} \log (1 - h e^{-ix}), \quad . \quad . \quad . \quad . \quad (35)$$

no constant of integration being required, since

$$\Sigma = -h^{-1}\log (1 - h) \quad \text{when } x = 0.$$

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* Enc. Brit. l. c. equation (43); Scientific Papers, iii. p. 98.

If now we put $h=1$,

$$\Sigma = -\log (1-e^{-ix})$$

$$= -\log\left(2 \sin\frac{x}{2}\right) + \tfrac{1}{2}i(x-\pi) + 2in\pi. \quad . \quad . \quad (36)$$

Thus

$$\frac{1}{ka} = i - \frac{2}{kR}\left\{-\log\left(2 \sin\frac{kR}{2}\right) + \tfrac{1}{2}i(kR-\pi) + 2in\pi\right\}. \quad (37)$$

If $kR = 2m\pi$, or $R = m\lambda$, where m is an integer, the logarithm becomes infinite and a tends to vanish *.

When R is very small, a is also very small, tending to

$$a = R \div 2 \log(kR). \quad . \quad . \quad . \quad (38)$$

The longitudinal density of the now approximately linear source may be considered to be a/R, and this tends to vanish. The multiplication of resonators ultimately annuls the effect at a distance. It must be remembered that the tuning of each resonator is supposed to be as for itself alone.

In connexion with this we may consider for a moment the problem in two dimensions of a linear resonator parallel to the primary waves, which responds symmetrically. As before, we may take at the resonator

$$\phi = 1, \quad d\phi/dr = 0.$$

As regards ψ, the potential of the waves diverging in two dimensions, we must use different forms when r is small (compared with λ) and when r is large †. When r is small

$$\psi/a = \left(\gamma + \log\frac{ikr}{2}\right)\left\{1 - \frac{k^2 r^2}{2^2} + \frac{k^4 r^4}{2^2 . 4^2} - \ldots\right\}$$

$$+ \frac{k^2 r^2}{2^2} - \frac{k^4 r^4}{2^2 . 4^2}(1+\tfrac{1}{2}) + \frac{k^6 r^6}{2^2 . 4^2 . 6^2}(1+\tfrac{1}{2}+\tfrac{1}{3}) - \ldots; \quad (39)$$

and when r is large,

$$\psi/a = -\left(\frac{\pi}{2ikr}\right)^{\frac{1}{2}} e^{-ikr}\left\{1 - \frac{1^2}{1 . 8ikr} + \frac{1^2 . 3^2}{1 . 2 . (8ikr)^2} - \ldots\right\} \quad (40)$$

By the same argument as for a point resonator we find, as the condition that no work is done at $r=0$, that the imaginary part of $1/a$ is $-i\pi/2$. For maximum resonance

$$a = 2i/\pi, \quad . \quad . \quad . \quad . \quad . \quad (41)$$

so that at a distance ψ approximates to

$$\psi = -\frac{\sqrt{\lambda}}{\pi\sqrt{r}} e^{-i(kr-\frac{1}{4}\pi)}. \quad . \quad . \quad . \quad (42)$$

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* Phil. Mag. vol. xiv. p. 60 (1907) ; Scientific Papers, vol. v. p. 409.
† 'Theory of Sound,' § 341.

Thus

$$2\pi r \cdot \mathrm{Mod}^2\psi = \frac{2\lambda}{\pi}, \quad \ldots \ldots \quad (43)$$

which expresses the width of primary wave-front carrying the same energy as is dispersed by the linear resonator tuned to maximum resonance.

A subject which naturally presents itself for treatment is the effect of a distribution of point resonators over the whole plane of the primary wave-front. Such a distribution may be either regular or haphazard. A regular distribution, *e. g.* in square order, has the advantage that all the resonators are similarly situated. The whole energy dispersed is then expressed by (29), but the interpretation presents difficulties in general. But even this would not cover all that it is desirable to know. Unless the side of the square (*b*) is smaller than λ, the waves directly reflected back are accompanied by lateral " spectra " whose directions may be very various. When $b < \lambda$, it seems that these are got rid of. For then not only the infinite lines forming sides of the squares which may be drawn through the points, but *a fortiori* lines drawn obliquely, such as those forming the diagonals, are too close to give spectra. The whole of the effect is then represented by the specular reflexion.

In some respects a haphazard distribution forms a more practical problem, especially in connexion with resonating vapours. But a precise calculation of the averages then involved is probably not easy.

If we suppose that the scale (*b*) of the regular structure is very small compared with λ, we can proceed further in the calculation of the regularly reflected wave. Let Q be one of the resonators, O the point in the plane of the resonators opposite to P, at which ψ is required; OP = x, OQ = y, PQ = r. Then if m be the number of resonators per unit area,

$$\psi = 2\pi m a \int_0^\infty y \, dy \, \frac{e^{-ikr}}{r},$$

or since $y \, dy = r \, dr$,

$$\psi = 2\pi m a \int_x^\infty e^{-ikr} \, dr.$$

The integral, as written, is not convergent: but as in the theory of diffraction we may omit the integral at the upper limit, if we exclude the case of a nearly circular boundary.

Thus

$$\psi = \frac{2\pi\, ma}{ik} e^{-ikx}. \quad \ldots \quad (44)$$

and

$$\mathrm{Mod}^2\,\psi = \frac{4\pi^2 m^2 \mathrm{A}^2}{k^2}. \quad \ldots \quad (45)$$

The value of A^2 is given by (19). We find, with the same limitation as above,

$$\Sigma\, \frac{\cos k\mathrm{R}}{\mathrm{R}} = 2\pi m \int_0^\infty \cos k\mathrm{R}\, d\mathrm{R} = 0,$$

$$\Sigma\, \frac{\sin k\mathrm{R}}{\mathrm{R}} = 2\pi m \int_0^\infty \sin k\mathrm{R}\, d\mathrm{R} = 2\pi m/k.$$

Thus

$$\mathrm{A}^2 = 1/(k + 2\pi m/k)^2$$

and

$$\mathrm{Mod}^2\,\psi = \frac{4\pi^2 m^2}{(k^2 + 2\pi m)^2}. \quad \ldots \quad (46)$$

When the structure is very fine compared with λ, k^2 in the denominator may be omitted, and then $\mathrm{Mod}^2\,\psi = 1$, that is the regular reflexion becomes total.

The above calculation is applicable in strictness only to resonators arranged in regular order and very closely distributed. It seems not unlikely that a similar result, viz. a nearly total specular reflexion, would ensue even when there are only a few resonators to the square wave-length, and these are in motion, after the manner of gaseous molecules; but this requires further examination.

In the foregoing investigation we have been dealing solely with forced vibrations, executed in synchronism with primary waves incident upon the resonators, and it has not been necessary to enter into details respecting the constitution of the resonators. All that is required is a suitable adjustment to one another of the virtual mass and spring. But it is also of interest to consider *free* vibrations. These are of necessity subject to damping, owing to the communication of energy to the medium, forthwith propagated away; and their persistence depends upon the nature of the resonator as regards mass and spring, and not merely upon the ratio of these quantities.

Taking first the case of a single resonator, regarded as bounded at the surface of a small sphere, we have to establish the connexion between the motion of this surface and the aerial pressure operative upon it as the result of vibration. We suppose that the vibrations have such a high degree of

persistence that we may calculate the pressure as if they were permanent. Thus if ψ be the velocity-potential, we have as before with sufficient approximation

$$\psi/a = \frac{1-ikr}{r}, \quad \frac{1}{a}\frac{d\psi}{dr} = -\frac{1}{r^2};$$

so that, if ρ be the radial displacement of the spherical surface, $d\rho/dt = -a/r^2$, and

$$\psi = -r(1-ikr)\,d\rho/dt. \quad . \quad . \quad . \quad (47)$$

Again, if σ be the density of the fluid and δp the variable part of the pressure,

$$\delta p = -\sigma\, d\psi/dt = \sigma r(1-ikr)d^2\rho/dt^2, \quad . \quad . \quad (48)$$

which gives the pressure in terms of the displacement ρ at the surface of a sphere of small radius r. Under the circumstances contemplated we may use (48) although the vibration slowly dies down according to the law of e^{int}, where n is not wholly real.

If M denotes the "mass" and μ the coefficient of restitution applicable to ρ, the equation of motion is

$$M\frac{d^2\rho}{dt^2} + \mu\rho + 4\pi\sigma r^3(1-ikr)\frac{d^2\rho}{dt^2} = 0, \quad . \quad . \quad (49)$$

or if we introduce e^{int} and write M' for $M+4\pi\sigma r^3$,

$$n^2(-M' + 4\pi\sigma kr^4 . i) + \mu = 0. \quad . \quad . \quad (50)$$

Approximately,

$$n = \sqrt{(\mu/M')} . \{1 + i . 2\pi\sigma kr^4/M'\};$$

and if we write $n = p + iq$,

$$p = \sqrt{(\mu/M')}, \quad q = p . 2\pi\sigma kr^4/M'. \quad . \quad . \quad (51)$$

If T be the time in which vibrations die down in the ratio of $e : 1$, $T = 1/q$.

If there be a second precisely similar vibrator at a distance R from the first, we have for the potential

$$\psi_2 = -\frac{r^2}{R} e^{-ikR} \frac{d\rho_2}{dt}, \quad . \quad . \quad . \quad . \quad (52)$$

and for the pressure due to it at the surface of the first vibrator

$$\delta p = \frac{\sigma r^2}{R} e^{-ikR} \frac{d^2\rho_2}{dt^2}. \quad . \quad . \quad . \quad (53)$$

The equation of motion for ρ_1 is accordingly

$$M\frac{d^2\rho_1}{dt^2} + \mu\rho_1 + 4\pi\sigma r^3 \left\{ (1-ikr)\frac{d^2\rho_1}{dt^2} + \frac{r\,e^{-ik\mathrm{R}}}{\mathrm{R}}\frac{d^2\rho_2}{dt^2} \right\} = 0;$$

and that for ρ_2 differs only by the interchange of ρ_1 and ρ_2. Assuming that both ρ_1 and ρ_2 are as functions of the time proportional to e^{int}, we get to determine n

$$n^2\{M' - 4\pi\sigma r^3 . ikr\} - \mu = \pm\, n^2\,.\,4\pi\sigma r^4 \mathrm{R}^{-1}e^{-ik\mathrm{R}},$$

or approximately

$$n = \sqrt{\frac{\mu}{M'}}\,.\,\left\{ 1 + \frac{2\pi\sigma r^4}{\mathrm{R}M'}\left(ik\mathrm{R} \pm e^{-ik\mathrm{R}}\right) \right\}. \quad . \quad (54)$$

If, as before, we take $n = p + iq$,

$$p = \sqrt{\frac{\mu}{M'}}\,.\,\left(1 \pm \frac{2\pi\sigma r^4}{\mathrm{R}M'}\cos k\mathrm{R} \right), \quad . \quad . \quad (55)$$

$$q = p\,.\,\frac{2\pi\sigma r^4}{\mathrm{R}M'}(k\mathrm{R} \mp \sin k\mathrm{R}). \quad . \quad . \quad . \quad (56)$$

We may observe that the reaction of the neighbour does not disturb the frequency if $\cos k\mathrm{R} = 0$, or the damping if $\sin k\mathrm{R} = 0$. When $k\mathrm{R}$ is small, the damping in one alternative disappears. The two vibrators then execute their movements in opposite phases and nothing is propagated to a distance.

The importance of the disturbance of frequency in (55) cannot be estimated without regard to the damping. The question is whether the two vibrations get out of step *while they still remain considerable*. Let us suppose that there is a relative gain or loss of half a period while the vibration dies down in the ratio of $e:1$, viz. in the time denoted previously by T, so that

$$(p_1 - p_2)\mathrm{T} = \pi.$$

Calling the undisturbed values of p and q respectively P and Q, and supposing $k\mathrm{R}$ to be small, we have

$$\frac{\mathrm{P}}{\mathrm{Q}}\frac{4\pi\sigma r^4}{\mathrm{R}M'} = \pi,$$

in which $\mathrm{Q}/\mathrm{P} = 2\pi\sigma k r^4/M'$. According to this standard the disturbance of frequency becomes important only when $k\mathrm{R} < 1/\pi$, or R less than λ/π^2. It has been assumed throughout that r is much less than R.

Terling Place, Witham.

XXVI. *Light Absorption and Fluorescence.*—Part II. *By* E. C. C. BALY, *M.Sc., F.R.S., Professor of Inorganic Chemistry in the University of Liverpool* *.

IN a previous paper † the existence of constant differences between the frequencies of absorption bands and fluorescence bands exhibited by many organic compounds was dealt with, and I showed that it was possible to account for these on the basis of the energy quantum theory. Several compounds are known each of which shows three absorption bands and at least one fluorescence band, and in these cases there exists a constant difference between the frequencies of the centres of these bands. I pointed out that the absorbed energy must be emitted again at some frequency which is characteristic of the molecular system, which frequency may be either in the visible spectrum, when we have fluorescence, or in the infra-red. Then on the energy quantum theory a single quantum absorbed at the higher frequency must be given out as a whole number of quanta at the lower frequency. If, therefore, ν_x be the frequency of the characteristic vibration in the infra-red, the energy can only be absorbed at the frequencies ν_1, ν_2, ν_3. &c., where ν_1, ν_2, ν_3, &c. are successive multiples of ν_x. Obviously, therefore, there must be a constant difference (ν_x) between the frequencies ν_1, ν_2, ν_3, &c., and this difference must equal the frequency of the infra-red vibration.

Since that paper was published a number of compounds have been accurately examined, and the above relation is found to hold good. These results will it is hoped be published in a separate communication. I omitted in the previous paper to point out that the existence of these constant frequency differences has also been noted by v. Kowalski in a paper dealing with the phosphorescence of a number of organic compounds ‡.

Two years ago a paper was published by Bjerrum §, in which he dealt with the short-wave infra-red absorption bands of certain compounds. He points out that if ν be the characteristic frequency of the atoms in a given molecule, then, if ν_r be the frequency of rotation of the molecules, three bands should be shown in the neighbourhood of the band ν. The frequencies of these will be $\nu - \nu_r$, ν, $\nu + \nu_r$ respectively. Since the central vibration is pure it will

* Communicated by the Author.
† *Phil. Mag.* xxvii. p. 632 (1914).
‡ *Phys. Zeit.* xii. 1911, p. 956.
§ Nernst, *Festschrift*, 1912, p. 90.

evidence itself only as a narrow absorption line, and will probably escape detection owing to the comparatively large width of slit necessary in infra-red work. The result will be that the band will appear to be double, each portion being broad since ν_r is the average rotational frequency of the molecules. Bjerrum further pointed out that on the energy quantum theory the rotational frequencies must have well defined values given by the formula $\nu_r = \dfrac{hn}{2\pi^2 I}$, where I is the moment of inertia, h the Planck constant, and n a whole number.

As a result of this, an absorption band in the short-wave region of the infra-red should consist of a series of maxima symmetrically distributed about a central line of frequency ν. Each pair of maxima will correspond to a definite rotational frequency of the molecules. Now Fräulein von Bahr has made very accurate measurements of the absorption band of water vapour at $6 \cdot 26\,\mu$, and found clear evidence of these pairs of maxima *. From these she calculated the wavelengths corresponding to the rotational frequencies, and showed an excellent agreement with the absorption bands as observed by Rubens and v. Wartenberg. Eucken † has shown that a still better agreement is obtained on the basis of there being two degrees of freedom possessed by the water molecule. The experimental evidence therefore most strongly supports Bjerrum's theory.

Now it is well known that the absorption bands of many organic compounds in the ultra-violet can be resolved into groups of fine lines, each group very frequently possessing a well marked head. It has occurred to me, if the bands in the short-wave infra-red region are due to atomic vibrations and those in the ultra-violet are due to electronic vibrations, that it should be possible to combine the two in the same way as has been done by Bjerrum. That is to say, if ν be the characteristic vibration frequency in the ultra-violet, then we should find pairs of absorption lines with frequencies equal to $\nu \pm \nu_x$, where ν_x stands for the frequencies of the short-wave infra-red bands. It is evident that the application of the theory can be tested on ultra-violet absorption bands with far greater accuracy than in the case of the infra-red bands for two reasons. Firstly, the measurement of the ultra-violet bands is much more accurate ; and, secondly, we know far more of the absorption bands in the short-wave region of the infra-red than of those in the long-wave region.

* Phil. Mag. xxviii. p. 71 (1914).
† *Deutsch. Phys. Ges., Verh.* xv. p. 1159 (1913).

Some preliminary support for the idea is gained from the fact that benzene exhibits nine absorption maxima which are obviously arranged symmetrically around a central position. This is also the case with several other compounds.

Again it follows that exactly the same structure should be found in the case of the fluorescence bands of the same substances. Finally, from what was stated in my previous paper, the central line of the fluorescence and absorption maxima should be consecutive multiples of a whole number which equals the frequency of one of the infra-red bands.

I have calculated the values of the ultra-violet absorption lines of one or two compounds, and find that they form in each case a series of pairs symmetrically distributed about a central line, and that the frequency of every infra-red band in the short-wave region has a corresponding line or pair of lines forming part of the structure of the ultra-violet absorption band. In short, the application of the Bjerrum conception to both ultra-violet and fluorescence bands is completely successful, and moreover the conclusions in my previous paper are entirely confirmed. This may be seen from the following.

Benzene.

Hartley [*] investigated the ultra-violet absorption band of benzene and published measurements of the wave-lengths of the component lines, which amount in number to about 90. He showed that these fine bands or lines seem to form ten groups, each with a well marked head. He gave the wave-lengths of these heads as 2670, 2630, 2590, 2523, 2466, 2411, 2360, 2335, 2326, and 2279 Ångströms. The values of $1/\lambda$ for these, expressed in four figures, are 3745, 3802, 3861, 3963, 4055, 4148, 4237, 4282, 4299, and 4388, respectively. Now it is obvious that the first four and the last five of these can be symmetrically distributed about the fifth with frequency $(1/\lambda)$ of 4055. The following table shows the arrangement of the ten bands and the values of the frequency differences.

In the third column are given the frequency differences between each line and the central line, and in the fourth column the means between the two values where such exist. The values of $1/\nu_x$ or the wave-lengths of the infra-red bands are given in the fifth column, while in the last column are to be found the wave-lengths of the absorption

bands as measured by Coblentz [*]. Four of the calculated bands were observed by Coblentz, and as can be seen the agreement is exceedingly good.

TABLE I.—Benzene.

λ in Angströms.	$1/\lambda$.	ν_x.	Mean ν_x.	Infra-red bands.	
				Calc.	Obs.
2670	3745	310		$3.23\,\mu$	$3.25\,\mu$
2630	3802	253	249	4.08	
2590	3861	194		5.15	
2523	3963	92	92.5	10.81	10.78
2466	4055	0			
2411	4148	93	92.5	10.81	10.78
2360	4237	182		5.50	5.41
2335	4282	227		4.40	4.40
2326	4299	244	249	4.08	
2279	4388	333		3.00	

On the other hand, there are altogether sixteen absorption bands shown by benzene between $3.0\,\mu$ and $15\,\mu$, which is the limit reached by Coblentz; and the question at once arises as to whether each of these gives rise to a corresponding line or pair of lines in the ultra-violet band when compounded with the central vibration $1/\lambda = 4055$. The complete list is given in Table II., and as can be seen every single infra-red band gives a pair of ultra-violet lines, except the band at $3.23\,\mu$, which only gives one line on the red side of the centre.

Certain of the calculated infra-red bands have not been observed by Coblentz, and they are included in the table because the corresponding ultra-violet pairs were given by Hartley as the heads of the ultra-violet band groups, and therefore the presumption would be in favour of these being important lines. Of course it is perfectly possible that the corresponding infra-red bands were missed by Coblentz owing to their being very narrow, but there is also another possible explanation. It must be remembered that only 36 out of the 200 benzene absorption lines are accounted for in the above table. It would seem likely that that in addition to the combining of the short-wave infra-red frequencies with the central frequency 4055, there is also coupled with these the rotation vibration of the molecules. If this were so then the probable result would be the existence of several

* Publications of the Carnegie Institution, Washington, No. 35 (1905).

series of absorption lines, each series starting from the
central line. There would be pairs of arithmetical series,

TABLE II.—Benzene absorption (Hartley).

λ in Ångströms.	$1/\lambda$.	ν_x.	Mean ν_x.	Infra-red bands.	
				Calc.	Obs.
2687	3722	333	333	3·00 μ	
A 2670	3745	310		3·23	3·25 μ
A 2630	3802	253	248·5	4·02	
2612	3828	227	228	4·38	4·40
2600	3847	208	208	4·80	4·90
A 2590	3861	194	194	5·15	
2582	3873	182	182	5·50	5·41
2567	3895	160	160	6·23	6·20
2560	3907	148	148	6·75	6·75
2553	3917	138	138	7·25	7·22
2546	3928	127	127	7·85	7·80
2538	3940	115	115	8·67	8·67
2529	3954	101	101·5	9·85	9·78
2527	3958	97	97	10·30	10·30
A 2523	3963	92	92·5	10·81	10·78
2519	3970	85	85	11·80	11·80
2516	3974	81	81	12·30	12·45
2514	3978	77	77	12·95	12·95
A 2466	4055	0			
2420	4132	77	77	12·95	12·95
2417	4136	81	81	12·30	12·45
2416	4140	85	85	11·80	11·80
A 2411	4148	93	92·5	10·81	10 78
2409	4152	97	97	10·30	10·30
2406	4157	102	101·5	9·85	9·75
2398	4170	115	115	8·67	8·67
2391	4182	127	127	7·85	7·80
2385	4193	138	138	7·25	7·25
2379	4203	148	148	6·75	6·75
2373	4215	160	160	6·23	6·20
A 2360	4237	182	182	5·50	5·50
2354	4249	194	194	5·15	
2346	4263	208	208	4·80	4·90
2334	4284	229	228	4·38	4·40
A 2326	4299	244	248·5	4·02	
A 2279	4388	333	333	3·00	

one on each side of the central line, and the result would be
the appearance of heads which mark the regions where
several lines of the different series happen to fall together.
On this explanation the heads will have no especial signifi-
cance in the present connexion, and so will not necessarily
be expected to correspond to bands in the short-wave infra-
red region. It is possible that in this combination of the
three vibrations electronic, atomic, and molecular (rotational),
the explanation is to be found of the structure of all band

spectra. This, however, cannot be entered into here. It is sufficient to say that it does not seem probable that there is any especial significance in the band heads in the absorption spectrum, and further that the whole of the remainder of the absorption bands of benzene beyond those given in the table may arise from a combination of the rotational frequencies of the molecules with the frequencies given in the table. These rotational frequencies certainly are of the right order of magnitude.

Turning now to the frequency of the central line 4055, it follows, if the deductions in the previous paper are sound, that this must be a whole multiple of the frequency of one of the infra-red bands. It is almost exactly 10×405*, which corresponds to a wave-length of $2 \cdot 47 \, \mu$, which corresponds to the band observed by Coblentz at $2 \cdot 49 \, \mu$. Now the next multiple of 405 is $9 \times 405 = 3645$, and this should form the central line of the fluorescence bands of benzene. The fluorescence of an alcoholic solution of benzene has accurately been measured by Dickson †, who found 6 bands with frequencies of 3436, 3537, 3631, 3733, 3795, and 3848. Now in order to compare these with the absorption measurements they must be corrected for the effect of the solvent which tends to shift the maxima towards the red. The values must therefore be increased by a few units. If 14 be added to the third frequency we have 3645, which should be the central line of the system. It may be assumed, therefore, that 14 should be added to all the values, and this is done in the third column of Table III. In the fourth column are given the frequency differences from the central line 3645, and in brackets are the mean values for the corresponding intervals found in Table II.

TABLE III.—Benzene fluorescence (Dickson).

λ in Ångströms.	$1/\lambda$.	$1/\lambda + 14$.	ν_x.
2910	3436	3450	195 (194)
2827	3537	3551	94 (92)
2754	3631	3645	0
2679	3733	3747	102 (101)
2635	3795	3809	164 (160)
2599	3848	3862	217 (208)

The agreement is remarkably good.

* The reason why this number is selected will be dealt with in a further communication.

† *Zeit. wiss. Phot.* x. p. 166 (1912).

It will be seen that in the cases of the compounds noted below there are included many pairs of absorption lines which correspond to infra-red bands that have not been observed. In the present state of our knowledge it is impossible to say whether these infra-red bands really do exist, or whether the absorption line pairs are due to the combination of the molecular rotational frequencies.

When the substitution products of benzene are considered some difficulty tends to arise, owing to the fact that the molecule becomes unsymmetrical. There is no doubt that the simplicity of the structure of the absorption spectrum of benzene is due to the symmetry of the molecule. The absorption spectrum of an alcoholic solution of benzene shows clear evidence of the symmetry. In toluene and its homologues much of this symmetry disappears, and therefore it cannot be expected that the absorption of the vapours of these substances should be so symmetrical. On the other hand, Miss Ewbank and I * showed that in the case of the disubstituted derivatives of benzene the para isomer is always the most symmetrical of the three, and this is well shown in the case of the three xylenes. As will be seen below, *p*-xylene shows remarkable evidence of symmetry, while in toluene, *o*-xylene, and *m*-xylene, the want of symmetry is evidenced by there being fewer absorption lines on the ultra-violet side of the central line.

Toluene.

The ultra-violet absorption of toluene vapour has been examined by Hartley †, Grebe ‡, and others. Hartley stated that the absorption lines resolved themselves into groups with heads at $\lambda = 2670$, 2633, 2605, 2587, 2530, 2471, and 2419. Grebe arranged the lines into a number of series with constant differences. The most accurate measurements of the absorption of toluene vapour have been published by Cremer §, who also arranged the lines in series of constant frequency differences.

In Table IV. are given Cremer's measurements of the toluene absorption lines, arranged in reference to the line at $\lambda = 2471$ taken as centre.

Again, in this case there is an exceedingly good agreement between the calculated and observed values of the infra-red bands, the latter being those given by Coblentz, whose paper is quoted as authority throughout. The lettering of the

* Trans. Chem. Soc. lxxxvii. p. 1347 (1905).
† Phil. Trans. ccviii. A. p. 475 (1908).
‡ *Zeit. wiss. Phot.* iii. p. 376 (1905).
§ *Zeit. wiss. Phot.* x. p. p. 349 (1912).

bands in the table has the following meaning :—The bands marked A are those which Cremer found to be the strongest, those marked B are those which according to Cremer form the heads of the series, while those marked H are the bands which Hartley considered to be the strongest.

TABLE IV.—Toluene absorption (Cremer).

λ in Ångströms.	$1/\lambda$.	ν_x.	Mean ν_x.	Infra-red bands.	
				Calc.	Obs.
ABH 2667	3749	298		$3\cdot36\,\mu$	$3\cdot34\,\mu$
2647	3778	269	271	$3\cdot69$	
AH 2635	3795	252	252	$3\cdot97$	$4\cdot00$
A 2630	3802	245		$4\cdot08$	
A 2615	3824	223	224	$4\cdot46$	
ABH 2603	3842	205		$4\cdot88$	
A 2600	3846	201	201	$4\cdot98$	
2595	3853	194		$5\cdot15$	$5\cdot10$
2589	3862	185	$186\cdot5$	$5\cdot38$	$5\cdot35$
AH 2585	3869	178		$5\cdot62$	$5\cdot51$
A 2580	3877	170		$5\cdot88$	$5\cdot80$
2572	3888	159		$6\cdot29$	$6\cdot20$
AB 2567	3895	152		$6\cdot58$	$\begin{cases} 6\cdot45 \\ 6\cdot70 \end{cases}$
2565	3899	146		$6\cdot85$	$6\cdot86$
2560	3906	141		$7\cdot09$	$7\cdot25$
2554	3915	132	131	$7\cdot63$	$7\cdot70$
A 2550	3922	125		$8\cdot00$	$8\cdot10$
2541	3936	111		$9\cdot01$	
2539	3939	108	$107\cdot5$	$9\cdot35$	$9\cdot27$
AB 2536	3943	104		$9\cdot61$	$9\cdot73$
H 2529	3954	93		$10\cdot75$	$10\cdot60$
2524	3961	86	86	$11\cdot60$	$11\cdot15$
2522	3965	82		$12\cdot20$	$12\cdot03$
2517	3974	73		$13\cdot70$	$13\cdot78$
B 2507	3988	59	61	$16\cdot39$	
2477	4037	10	$10\cdot5$	$95\cdot24$	
H 2471	4047	0			
A 2464	4058	11	$10\cdot5$	$95\cdot24$	
2433	4110	63	61	$16\cdot39$	
BH 2420	4133	86	86	$11\cdot60$	$11\cdot15$
B 2407	4154	107	$107\cdot5$	$9\cdot30$	$9\cdot27$
B 2394	4177	130	131	$7\cdot63$	$7\cdot70$
2359	4235	188	$186\cdot5$	$5\cdot38$	$5\cdot35$
2354	4248	201	201	$4\cdot98$	
2341	4272	225	224	$4\cdot46$	
2326	4299	252	252	$3\cdot97$	$4\cdot00$
2315	4320	273	271	$3\cdot69$	

Only two of Coblentz's toluene bands are not accounted for, namely, those at $\lambda = 8\cdot40$ and $8\cdot53\,\mu$. Now Cremer in his series of lines notes that certain members are absent, and one of these missing lines should have a wave-length of $\lambda = 2545$ Ångströms and a frequency of $1/\lambda = 3929$. This gives a value of $\nu_x = 118$, which corresponds to a band in the

infra-red at $\lambda = 8\cdot48\,\mu$, an almost exact mean of the two bands observed at $8\cdot40$ and $8\cdot53\,\mu$.

It is interesting to note that the central line at $1/\lambda = 4047$ is very nearly the same as that of benzene (4055). Now $4047 = 10 \times 405$ very nearly, and therefore $9 \times 405 = 3645$ should again be the central line of the fluorescence maxima. If Dickson's values for the fluorescence of toluene be taken, it is clear that the maximum at 3650 must be the centre of the system. The maxima can be arranged as in Table V., the figures in brackets again showing the corresponding values of ν_x obtained in the absorption band. The accuracy of determination of the wave-lengths of fluorescence maxima is not very great, and if the correction for solvent be applied here there appears to be an error of about 9 units in the value of $1/\lambda$ for the central line. This is well within the limit of experimental error.

TABLE V.—Toluene fluorescence (Dickson).

λ in Ångströms.	$1/\lambda$.	ν_x.
2886	3465	185 (186·5)
2809	3561	89 (86)
2740	3650	0
2676	3737	87 (86)
2646	3779	129 (131)
2622	3814	164 (159)

Again a very good agreement is shown between the values obtained from the absorption and fluorescence spectra.

The want of symmetry of the toluene molecule is well shown by the fact that out of the 19 infra-red bands only 5 give pairs of absorption lines, the remainder being evidenced only by lines on the red side of the centre.

p-Xylene.

Although the vapour absorption spectrum of *p*-xylene was investigated by Hartley, more accurate measurements have been published by Mies[*], who showed that the fine lines can very readily be arranged in series. He observed in the spectrum a certain number of strong lines which he denoted by A, and also a number of slightly less strong lines which he denoted by B. The A lines and the B lines form two series with constant frequency differences. Then, further, he found other lines, the frequencies of which differ by definite amounts from the frequencies of the members of the

[*] *Zeit. wiss. Phot.* vii. p. 357 (1909).

A and B series. He thus established four series which he denoted by A, C, B, D, the C and the D series being connected with the A and the B series respectively. In Table VI. are given the absorption lines of p-xylene arranged in reference to the line $1/\lambda = 3869$ as centre, and the letters refer to Mies' classification.

TABLE VI.—p-Xylene absorption (Mies).

λ in Ångströms.	$1/\lambda$.	ν_x.	Mean ν_x.	Infra-red bands.	
				Calc.	Obs.
2814	3554	315	316	$3 \cdot 17 \, \mu$	$3 \cdot 25 \, \mu$
2800	3571	298	298	$3 \cdot 36$	$3 \cdot 38$
A 2785	3591	278	$277 \cdot 5$	$3 \cdot 60$	
C 2771	3609	260	258	$3 \cdot 88$	
B 2757	3627	242	241	$4 \cdot 15$	
D 2744	3644	225	222	$4 \cdot 50$	
A 2722	3673	196	$196 \cdot 5$	$5 \cdot 09$	
2717	3680	189		$5 \cdot 28$	$5 \cdot 30$
C 2709	3691	178	178	$5 \cdot 62$	
B 2695	3710	159	160	$6 \cdot 25$	$\left\{ \begin{array}{c} 6 \cdot 10 \\ 6 \cdot 35 \end{array} \right.$
2691	3716	153		$6 \cdot 55$	$6 \cdot 55$
2685	3724	145		$6 \cdot 90$	$6 \cdot 90$
D 2682	3728	141	$140 \cdot 5$	$7 \cdot 12$	
2680	3731	138		$7 \cdot 25$	$7 \cdot 25$
A 2664	3753	116	117	$8 \cdot 55$	$8 \cdot 60$
2661	3758	111	111	$9 \cdot 04$	$9 \cdot 05$
2657	3764	105	104	$9 \cdot 60$	$9 \cdot 62$
C 2650	3773	96	97	$10 \cdot 31$	$10 \cdot 20$
2643	3785	84	84	$11 \cdot 90$	$11 \cdot 90$
B 2637	3792	77	78	$12 \cdot 82$	$12 \cdot 58$
D 2624	3811	58	59	$16 \cdot 95$	
A 2611	3830	39	39	$25 \cdot 64$	
C 2598	3850	19	$19 \cdot 5$	$51 \cdot 28$	
B 2584	3869	0			
D 2571	3889	20	$19 \cdot 5$	$51 \cdot 28$	
A 2558	3908	39	39	$25 \cdot 64$	
C 2545	3929	60	59	$16 \cdot 95$	
B 2533	3948	79	78	$12 \cdot 82$	$12 \cdot 58$
2530	3953	84	84	$11 \cdot 90$	$11 \cdot 90$
D 2521	3967	98	97	$10 \cdot 31$	$10 \cdot 20$
2517	3973	104	104	$9 \cdot 60$	$9 \cdot 62$
2512	3980	111	111	$9 \cdot 04$	$9 \cdot 05$
A 2508	3987	118	117	$8 \cdot 55$	$8 \cdot 60$
C 2494	4009	140	$140 \cdot 5$	$7 \cdot 12$	$\left\{ \begin{array}{c} 7 \cdot 25 \\ 6 \cdot 90 \end{array} \right.$
B 2483	4028	161	160	$6 \cdot 25$	$\left\{ \begin{array}{c} 6 \cdot 35 \\ 6 \cdot 10 \end{array} \right.$
D 2471	4048	178	178	$5 \cdot 62$	
A 2460	4066	197	$196 \cdot 5$	$5 \cdot 09$	
2447	4087	218	222	$4 \cdot 50$	
B 2434	4109	240	241	$4 \cdot 15$	
2425	4124	255	258	$3 \cdot 88$	
A 2412	4146	277	$277 \cdot 5$	$3 \cdot 60$	
C 2400	4167	298	298	$3 \cdot 36$	$3 \cdot 38$
B 2389	4186	317	316	$3 \cdot 17$	$3 \cdot 25$

Again, every infra-red band is accounted for, and also the greater symmetry of the molecule is shown by the fact that out of the 14 infra-red bands 11 give rise to pairs of absorption lines.

The frequency of the central line $3869 = 15 \times 258$ almost exactly, and $14 \times 258 = 3612$ should be the central line of the fluorescence. Only 4 fluorescence bands were observed by Dickson, and the frequencies of these should arrange themselves symmetrically round this as centre. The four frequencies when corrected for solvents are 3504, 3584, 3665, and 3744, and these obviously can be arranged round 3624 as centre as shown in Table VII.

TABLE VII.—p-Xylene fluorescence (Dickson).

λ in Ångströms.	$1/\lambda$.	$1/\lambda + 12$.	ν_x.
2865	3492	3504	120 (117)
2801	3572	3584	40 (39)
2739	3653	3665	41 (39)
2681	3732	3744	120 (117)

Now, $3624 = 14 \times 258 \cdot 8$, and the fundamental interval is therefore very near that of the absorption band system (258). The small number of the fluorescence bands makes it impossible to arrive at greater accuracy.

The absorption lines and fluorescence maxima can also be arranged in the same way for o-xylene and m-xylene, and they are shown in Tables VIII., IX., X., and XI. In these tables certain lines are marked A or F. Those marked A are the lines which Hartley considered to be the heads of the band groups, while those marked F give the same values of ν_x as appear in the fluorescence spectrum. The wavelengths of the lines are taken from Mies' paper *.

The frequency of the central line $3909 = 13 \times 300 \cdot 7$. The next multiple is $12 \times 300 \cdot 7 = 3608$, which may be taken as the centre of the fluorescence bands. In Table IX. the frequencies of the fluorescence bands are increased by 13 units to correct for the effect of the solvent.

* *Zeit. wiss. Phot.* viii. p. 287 (1910).

TABLE VIII.   *o*-Xylene absorption (Mies).

λ in Ångströms.	$1/\lambda$.	ν_x.	Mean ν_x.	Infra-red bands.	
				Calc.	Obs.
2777	3601	308		$3{\cdot}25\,\mu$	$3{\cdot}25\,\mu$
2770	3610	299		3·33	3·38
F 2730	3663	246		4·07	
F 2699	3705	204		4·90	
2691	3716	193		5·18	5·24
A 2683	3727	182		5·49	
A 2668	3748	161		6·21	6·20
2666	3751	158		6·33	6·30
2659	3761	148		6·74	{ 6·75 6·86
2654	3768	141	141	7·09 }	7·25
2650	3774	135		7·41 }	
A 2547	3778	131		7·63	
A 2633	3798	111		9·01	8·92
2628	3805	104		9·64	{ 9·50 9·78
2624	3811	98	97	10·31	10·20
2620	3817	92	91·5	10·91	
2607	3836	73	75	13·33	13·60
A 2601	3845	64		15·63	
A 2585	3869	40		25·00	
F 2572	3888	21		47·62	
A 2558	3909	0			
A 2527	3957	48		20·83	
2509	3986	77	75	13·33	13·60
2500	4000	91	91·5	10·91	
2497	4005	96	97	10·31	10·20
2474	4042	141	141	7·09	7·25

TABLE IX.   *o*-Xylene fluorescence (Dickson).

λ in Ångströms.	$1/\lambda$.	$1/\lambda+13$.	ν_x.
3135	3190	3203	405
3038	3292	3305	303 (299)
2986	3349	3362	246 (246)
2896	3453	3466	142 (141)
2798	3574	3587	21 (21)
2713	3686	3699	91 (91)
2680	3731	3744	141 (141)
2636	3794	3807	199 (204)
2603	3842	3855	247 (246)

It is to be noted that the fundamental frequency 301 appears both in the absorption and fluorescence spectra.

TABLE X.—*m*-Xylene absorption (Mies).

λ in Angströms.	1/λ.	ν_x.	Mean ν_x.	Infra-red bands.	
				Calc.	Obs.
2802	3569	295		3·39 μ	3·38 μ
2721	3675	189		5·29	5·25
F 2716	3682	182	181	5·52	
2703	3699	165	163·5	6·12	6·20
2694	3712	152		6·58	6·77
F 2687	3722	142	142	7·04	
2684	3726	138		7·25	7·25
2668	3748	116		8·62	8·70
2663	3755	109		9·17	9·17
2658	3762	102	103	9·70	9·68
2655	3767	97		10·30	10·20
2648	3776	88	87·5	11·43	11·42
2640	3788	76	74·5	13·42	13·00
F 2601	3645	19	20	50·00	
2588	3864	0			
F 2574	3885	21	20	50·00	
2540	3937	73	74·5	13·42	13·00
2531	3951	87	87·5	11·43	11·42
2520	3968	104	103	9·70	9·70
F 2496	4006	142	142	7·04	
2484	4026	162	163·5	6·12	6·20
F 2473	4044	180	181	5·52	

The central line 3864 is almost exactly 13×297, and $12 \times 297 = 3564$, which should be the centre of the fluorescence. Dickson only finds three maxima of fluorescence, and they all lie on the ultra-violet side of 3564. If this be correct, then allowing 14 units for the effect of the solvent the fluorescence bands may be arranged as in Table XI.

TABLE XI.—*m*-Xylene fluorescence (Dickson).

λ in Angströms.	1/λ.	1/λ+14.	ν_x.
2802	3569	3583	19 (20)
2715	3683	3697	133 (142)
2685	3724	3738	174 (181)

It is, however, manifestly impossible to draw any definite conclusion from only three maxima.

There can be little doubt from the above results that the conception of combining the frequencies of the short-wave infra-red bands with those of central lines of absorption and fluorescence bands is justified. In the five substances dealt

with, every single infra-red band observed by Coblentz, with
two possible exceptions, is represented by either one or two
lines in the ultra-violet absorption band, and further, the
agreement between the calculated and observed values of the
infra-red bands is remarkable.

The general conception can be put to a very severe test in
the following way. Dickson found in the fluorescence
spectrum of naphthalene 14 well-defined maxima which are
very regularly arranged. In fact their frequencies may be
expressed by the general formula

$$1/\lambda = 3326 - 47\cdot12 \times n,$$

where n is 0, 1, 2, ... 13. He finds small differences
between the observed values and those calculated from the
formula, especially in the case of the band with the smallest
frequency. It would seem, therefore, that in making any
calculations from the frequencies, it would be preferable to
use the values obtained from the formula. Now the absorp-
tion spectrum of naphthalene in the infra-red region has not
been observed, and the only fact known about it is that
Coblentz found a band at $\lambda = 3\cdot25\,\mu$ for a solution of the
compound in carbon tetrachloride. It is not possible, there-
fore, to check the values of frequency differences against
infra-red measurements. Since the fluorescence bands are
very symmetrically arranged, it is possible accurately to
calculate the frequency differences from the central line.
This central frequency must be a multiple of the funda-
mental frequency, and the next higher multiple should form
the centre of the ultra-violet absorption band. From this
new central frequency, by making use of the frequency
differences found in the fluorescence spectrum, it should be
possible to calculate the frequencies of the lines in the ultra-
violet absorption band.

In Table XII. are given the frequencies of the fluorescence
maxima of naphthalene as corrected by Dickson, and arranged
symmetrically with respect to the mean frequency $1/\lambda = 3020$,
together with the frequency differences.

The calculated values of the infra-red bands are given so
that when this region is investigated, the observed values
may be compared.

Now the central frequency $3020 = 302 \times 10$, and as there-
fore the fundamental frequency of naphthalene is 302,
the central frequency of the absorption band must be
$302 \times 11 = 3322$. In order to calculate the frequencies of
the absorption lines, we thus use $3322 \pm \nu_x$, the values of
ν_x being those given in Table XII.

TABLE XII.—Naphthalene fluorescence (Dickson).

$1/\lambda$.	ν_x.	Calculated Infra-red bands.
2714	306	$3\cdot27\,\mu$
2761	259	$3\cdot86$
2808	212	$4\cdot72$
2855	165	$6\cdot06$
2902	118	$8\cdot48$
2949	70·5	$14\cdot2$
2996	23·5	$42\cdot6$
(3020)		
3043	23·5	$42\cdot6$
3090	70·5	$14\cdot2$
3138	118	$8\cdot48$
3185	165	$6\cdot06$
3232	212	$4\cdot72$
3279	259	$3\cdot86$
3326	306	$3\cdot27$

The absorption of naphthalene vapour has been investigated by Purvis, who finds that the bands shown by the alcoholic solution are not resolved into fine lines. It is necessary, therefore, to make use of the solution spectrum of naphthalene for the present comparison. This spectrum has been measured by several observers[*], and Mr. F. C. Guthrie, in my laboratory, has kindly repeated the observations, using the new Hilger ultra-violet spectrophotometer, the accuracy of which far exceeds that of the old method of qualitative measurement.

In Table XIII. the first column shows the values of ν_x obtained from the fluorescence bands and given in Table XII. The second column contains the calculated frequencies of the absorption bands, while the corresponding wave-lengths appear in the third column. In the fourth column are given Mr. Guthrie's measurements.

The agreement between calculated and observed values is exceedingly good in view of the fact that there are no infra-red measurements against which the frequency differences (ν_x) can be checked. Certain of the calculated absorption bands do not appear in the solution spectrum, and the broad band at $\lambda = 2965$ does not seem to divide. One more absorption band has been observed at $\lambda = 2670$ beyond those that have their counterpart in the fluorescence spectrum. It

[*] Hartley, Trans. Chem. Soc. xxxix. p. 153 (1881); xlvii. p. 685 (1885). Baly and Tuck, Trans. Chem. Soc. xciii. p. 1902 (1908). Purvis, Trans. Chem. Soc. ci. p. 1315 (1912).

TABLE XIII.—Naphthalene absorption.

ν_x.	$1/\lambda$.	Wave-lengths in Ångströms.	
		Calc.	Obs.
306	3016	3311	
259	3063	3265	
212	3110	3215	3218
165	3157	3168	3158
118	3204	3121	3118
71	3251	3076	
23	3299	3031	3025
0	(3322)		
23	3345	2990 ⎫	2965
71	3393	2945 ⎬	
118	3440	2907 ⎭	
165	3487	2868	2867
212	3536	2828	2830
259	3581	2793	2798
306	3628	2757	2759
			2670

may be claimed that the above calculation completes the evidence and confirms the theory here put forward of the complex structure of ultra-violet absorption bands.

Two interesting points may be noted, one of which is the agreement of the only observed infra-red band of naphthalene with the calculated value, and the other is the fundamental frequency of 302. This frequency is practically the same as that of *o*-xylene, which is 301. Naphthalene can be looked upon as containing ortho substituted benzene rings, and it would seem therefore as if 301 or 302 might prove to be the fundamental frequency of ortho disubstituted benzene compounds.

There is no doubt that it should also be possible on the present theory to explain the phosphorescence spectra as observed by v. Kowalski[*] and by Goldstein[†] with certain organic compounds. Both these authors investigated the phosphorescence of the solid substance at very low temperatures, and we have no knowledge of the shift of the bands under these conditions as compared with the vapour. It is impossible, therefore, to calculate the frequencies from these authors' measurements in the way adopted above.

The following substances may be selected, namely, benzene and *p*-xylene, both of which were investigated by v. Kowalski,

* *Phys. Zeit.* xii. p. 956 (1911).

† *Phys. Zeit.* xii. p. 614 (1911); *Deutsch. Phys. Ges., Verh.* xiv. pp. 33 & 493 (1912).

and the latter also by Goldstein. The fundamental frequencies
of these compounds are 405 and 258 respectively. The
simplest method of calculation is to find whether the phos-
phorescence maxima can be arranged in each case with
reference to a multiple of the fundamental frequency, due
regard being paid to the fact that the phosphorescence
maxima are certain to be moved towards the red. The
accuracy of measurement reached by v. Kowalski and
Goldstein is only about 25 Ångströms, and therefore the
frequencies are only expressed in three figures. But in
spite of this, it is clear that the same relation holds good
here also.

Thus in benzene the frequencies of the phosphorescence
maxima can be arranged symmetrically with respect to
$1/\lambda = 242$, as shown in Table XIV., together with the cor-
responding values of ν_x (in brackets) found in the absorption
band.

TABLE XIV.—Benzene phosphorescence
(v. Kowalski).

$1/\lambda.$	$\nu_x.$
230	12 (12·7)
233	9 (9·2)
239	3
242	0
249	7 (7·7)
252	10 (10·2)
260	18 (18·4)
263	21 (20·8)
270	28
274	32 (31·8)
280	38
284	42 (40·5)
289	47
295	53

It may be pointed out that the frequency difference of 47
corresponds very nearly with the infra-red band at $2·18\,\mu$
$(1/\lambda = 46)$.
We thus have for the fundamental frequency of benzene
the following values :—

Phosphorescence . . $6 \times 403·3$
Fluorescence . . . 9×405
Absorption . . . . 10×405

In the case of *p*-xylene the following values are obtained (Table XV.).

TABLE XV.—*p*-Xylene.

Phosphorescence (v. Kowalski).			Cathodoluminescence (Goldstein).	
$1/\lambda.$	$\nu_x.$	Mean $\nu_x.$	$1/\lambda.$	$\nu_x.$
234	22	22　(22·2)	176	30 (29·8)
239	17	17·5 (19 and 16)	180	26 (26)
243	13	13·5 (13·8)	184	22 (22·2)
249	7	8　(7·8)	188	18 (19)
253	3	2·5	192	14 (14)
(256)	0		196	10 (10·5)
258	2	2·5	200	6 (5·9)
265	9	8　(7·8)	205	0
270	14	13·5 (13·8)	208	2 (1·95)
274	18	17·5 (16 and 19)	212	6 (5·9)
282	26	?	Central line 205·6.	
Central line 256.				

It is possible that there is an error in **v. Kowalski's** measurement of the last maximum on his list. We thus have for the fundamental frequency of *p*-xylene the following values :—

$$\text{Cathodoluminescence}\quad 8 \times 257$$
$$\text{Phosphorescence}\quad .\quad .\quad 10 \times 256$$
$$\text{Fluorescence}\quad .\quad .\quad .\quad 14 \times 258$$
$$\text{Absorption}\quad .\quad .\quad .\quad .\quad 15 \times 258$$

It is manifestly impossible to expect much accuracy from the values of the phosphorescence maxima, seeing that the measurements themselves of these are far from accurate, but they certainly seem to give considerable support to the theory put forward in this paper, a theory which would appear to be proved correct from the absorption and fluorescence measurements.

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XXVII. *Anomalous Zeeman Effect in Satellites of the Violet Line* (4359) *of Mercury. By* H. NAGAOKA, *Professor of Physics, and* T. TAKAMINE, *Graduate in Physics, Imperial University, Tokyo* *.

[Plates III. & IV.]

THE changes wrought by magnetic fields on the satellites of spectrum lines are generally different from those observed in the principal line, both as regards the modes of separation and in the distribution of intensities among the different components. The effect is in these respects mostly anomalous, if we follow the course of satellites to strong fields, although some regularity usually observed in simple lines may still be traced in fields of a few thousand gauss. The present paper is a continuation of the experiments † made on the satellites of the green and violet lines λ 5461 and λ 4047 respectively, to those of λ 4359. The study of this line is specially interesting as it is accompanied by more than ten satellites, whose displacements in magnetic fields are so diverse, that different cases of anomalies already noticed in the satellites of two lines above mentioned are also found in those of λ 4359.

The method of observation was exactly the same as that already described in our former paper, so that it will be unnecessary to enter into its details. Briefly speaking, the position of satellites with respect to the principal line in magnetic fields was determined mostly from photograms taken with an echelon grating, and the course of the curves giving the transition of the satellites was traced from those obtained in heterogeneous fields. Some doubtful cases were also examined in the photograms of interference points, obtained either by combining the echelon grating with the Lummer-Gehrcke plate or with the Fabry-Perot interferometer. Owing to the great complexity in the distribution of the satellites, it was only after various examinations of 180 photograms that the displacements of the satellites were finally settled.

Typical photograms showing the lines in uniform and heterogeneous fields are shown in Pl. III.

Fig. 1 *a* and fig. 1 *b* show comparisons of the lines λ 5461

and $\lambda 4359$ in a field of 15,500 gauss. Figs. 2 a, 2 b, 2 c are enlarged photograms of the p- and s-components taken in fields of 6300, 14,600, and 20,300 gauss respectively. The general appearance of the lines in heterogeneous fields is shown in fig. 3 a and fig. 3 b, of which the latter is more enlarged than the former. Faint lines are not distinctly seen in photographic reproductions, so that these figures only serve to illustrate the complex appearance of the satellites with reference to the principal lines.

Principal Line.—It is generally assumed that the so-called principal line is simple and has finite breadth ; it was on this supposition that we have measured the Zeeman effect of satellites belonging to the lines $\lambda 5461$ and $\lambda 4047$. This is by no means always the case. Janicki [*] showed that the principal line of $\lambda 5461$ has fine structure and can be resolved into five lines. We recently found that the principal lines of $\lambda 4359$ and $\lambda 4047$ are of similar nature, and cannot be treated as a single broad line. This fact will doubtless have an important bearing on the Zeeman effect. It will therefore not be out of place to give a brief sketch of the result, reserving the detailed description of the resolution for another place.

By combining the echelon grating with a Lummer-Gehrcke plate, both of resolving power slightly exceeding 4×10^5, we [†] have shown that there are two satellites $+17$ and -23 m.Å.U. very near the principal line $\lambda 4359$. The interval between -23 and the principal is, however, so vague, that the presence of a cluster of lines seemed to us very probable. By combining an echelon grating or a Lummer-Gehrcke plate with a sliding Fabry-Perot interferometer, and making the air-plate about 5 cm. thick, thereby utilizing a resolving power of about 2×10^6, we found that the assumed principal line is composed of a group of three strong lines, the consecutive distance between them being about 6 m.Å.U. The middle line of the triplet may be considered as the principal. When the analysing power of the interferometer is not sufficient to resolve the principal line, the mean point appears displaced by about 3 m.Å.U. towards the side of longer wave-length, from that given in our investigation concerning the constitution of mercury lines. The reason why Janicki did not observe the fine structure of the violet lines must be ascribed to the low resolving power of his instruments.

* Janicki, *Ann. d. Phys.* xxxix. p. 439 (1912).
† Nagaoka and Takamine Proc. Phys. Soc. xxv. p. 1 (1912).

We take this opportunity of filling in the omissions which we have made in our former communication on the Zeeman effect of $\lambda\,5461$ and $\lambda\,4047$. The principal lines have fine structure, as given in fig. 4, fig. 5, fig. 6, which indicate the position as well as the intensity of different lines forming a triplet of the second subordinate series of mercury. The new lines are marked with asterisks.

Fig. 4. $\lambda : 5461$
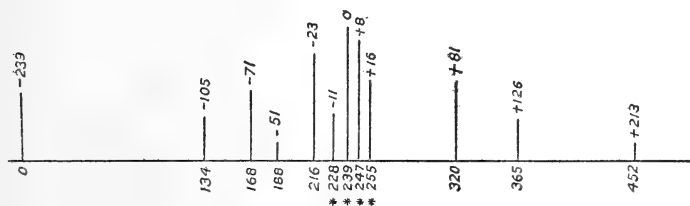
Fig. 5. $\lambda : 4359$
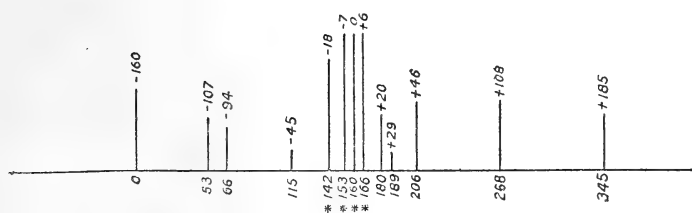
Fig. 6. $\lambda : 4047$
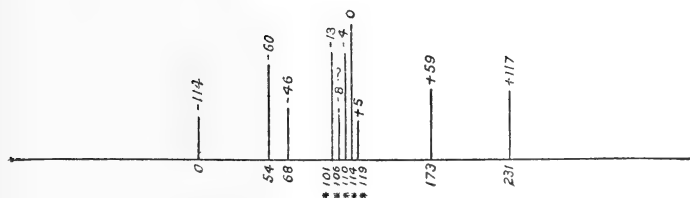
The result for $\lambda\,5461$ is almost identical with that of Janicki. He considers the principal line as a doublet of equal intensity, but according to our experiments, the one towards the violet appears stronger than those towards the red.

R 2

In order to avoid the ambiguity in the position of the principal line, the position of satellites is sometimes referred to that lying farthest towards the violet. But we believe that finer structures will no more be forthcoming, and in discussing the Zeeman effect especially, it is convenient to refer the position of satellites to that of the principal line.

As the examination of this fine group of lines is only possible so long as the light is quiet and steady, the Zeeman effect of each of the lines forming a cluster is almost impossible to follow in the present stage of our experiments. Owing to this circumstance, what we consider as the magnetic separation of the principal line refers to that of the cluster. Whether the structure remains unaltered in magnetic fields or not, seems to be an important problem, but special means and arrangements will be required to decide the question.

According to Runge and Paschen, the principal line $\lambda\,4359$ is divided into a regular sextet, following the rule

$$\pm\frac{a}{2}, \quad \pm\frac{3}{2}a, \quad \pm 2a.$$ This is only approximately fulfilled.

To test the deviation, we compared the separation with that of the green line, which almost exactly obeys the rule,

$$0, \quad \pm\frac{a}{2}, \quad \pm a, \quad \pm\frac{3}{2}a, \quad \pm 2a.$$ These two lines were photographed side by side in the same field (Pl. III. fig. 1 *a* and fig. 1 *b*). By increasing the field gradually, the following results were obtained :—

H in gauss.	$\pm\delta\lambda_1(P_{\pm 1})$.	$\pm\delta\lambda_2(P_{\pm 2})$.	$\pm\delta\lambda_3(P_{\pm 3})$.	$\dfrac{\delta\lambda_2}{\delta\lambda_1}$.	$\dfrac{\delta\lambda_3}{\delta\lambda_1}$.
13900	62 m.Å.U.	178 m.Å.U.	241 m.Å.U.	2·88	3·90
18200	81 ,,	240 ,,	324 ,,	2·96	4·00
21000	94 ,,	267 ,,	365 ,,	2·84	3·88
22800	102 ,,	300 ,,	400 ,,	2·94	3·92
24400	109 ,,	316 ,,	429 ,,	2·90	3·94

The branches of the sextet are designated by the letters P_{+1}, P_{+2}, P_{+3} and P_{-1}, P_{-2}, P_{-3}, of which P_{+1} and P_{-1} vibrate parallel (p), and the rest perpendicular (s) to the

magnetic field. If Runge's rule be strictly obeyed, $\dfrac{\delta\lambda_2}{\delta\lambda_1} = 3$, and $\dfrac{\delta\lambda_3}{\delta\lambda_1} = 4$. The agreement is not therefore so close as with the green line. Whether this discrepancy is to be attributed to the fine structure of the assumed principal line or not is an important question. When we recollect that the green line has similar structure and still obeys Runge's rule, we cannot at once answer the question positively.

Satellites.—The displacements of the satellites were measured by taking the branches of the sextet as reference lines. Unfortunately the finite breadth of these branches makes the line somewhat vague, so that micrometric measurements were not entirely free from the error of pointing, especially in low fields.

As already noticed in our former paper, the p-components are simpler than the s-components. The distribution of lines in the photograms of $\lambda\,4359$ is very intricate, and the tracing of points lying on the curve representing the displacements presents extreme difficulty, but we believe that the principal feature of the mode of separation has been deciphered, except for faint satellites or for those lying very near the quartet $P_{\pm2}$, $P_{\pm3}$, of the principal lines, which are far superior in intensity and obscure the traces of satellites.

The general feature of the p-components is shown in fig. 7, Pl. IV., and of the s-components in fig. 8, Pl. IV. It will be noticed at a glance that the Zeeman effect of the satellites is almost without exception anomalous. As was already shown with the lines $\lambda\,5461$ and $\lambda\,4047$, the anomaly appears either as a dissymmetry in the intensity of the displaced lines, or as deviations from the law of linear proportionality of the amount of displacement to the magnetic field. These two features are also characteristic of the satellites of the violet line $\lambda\,4359$.

The observations of the displacements of different satellites are given in the following tables. The lines in which the displacement $\delta\lambda$ is proportional to the field H are first tabulated. When this condition is not satisfied, the displacement is generally represented by an hyperbolic curve, which is given by

$$H^2 = a\delta\lambda + b\delta\lambda^2.$$

Sometimes $b = 0$, and the curve becomes parabolic.

I.—SIMPLE DISPLACEMENTS.

(−160)

s-component.

+ side.

H.	δλ.	$\frac{\delta\lambda}{H}\times10^2$.
1300	18	(1·38?)
2000	21	1·05
4300	43	1·00
5100	46	0·90
9900	96	0·97
10200	101	0·99
10800	106	0·98
11400	113	0·99

(−107)

p-component.

H.	δλ.	$\frac{\delta\lambda}{H}\times10^2$.
10800	0	0
11300	0	0
12700	4	0

(−18)

p-component. −side.			s-components. + side (outer).			− side (inner).			+ side.		
H.	δλ.	$\frac{\delta\lambda}{H}\times10^2$.	H.	δλ.	$\frac{\delta\lambda}{H}\times10^2$.	H.	δλ.	$\frac{\delta\lambda}{H}\times10^2$.	H.	δλ.	$\frac{\delta\lambda}{H}\times10^2$.
2300	−17	−0·74	1800	−53	(2·95?)	1300	−27	(−2·08?)	2800	34	1·18
2900	−20	−0·69	3300	−84	2·55	4100	−78	−1·90	3300	37	1·12
3300	−32	−0·97	5100	−126	2·47	5100	−96	−1·88	6500	77	1·18
4200	−37	−0·88	10200	−255	2·50	10800	−203	−1·88	7400	83	1·12
7600	−47	−0·62	10800	−265	2·45	12300	−234	−1·90	10200	119	1·17
12800	−106	−0·83	11000	−270	2·45	14500	−274	−1·89	14200	171	1·21
			11400	−279	2·45	16700	−307	−1·84	16400	201	1·22
			14300	−354	2·48	19200	−356	−1·86	18000	220	1·22
			16500	−398	2·42	20600	−379	−1·84	23000	279	1·21

(+20)

s-component.

−side.

H.	δλ.	$\frac{\delta\lambda}{H}\times10^2$.
2200	−30	1·36
7400	−101	1·37
14500	−191	1·32
16000	−211	1·32

(+46)

p-components.

− side.			+ side.		
H.	δλ.	$\frac{\delta\lambda}{H} \times 10^2$	H.	δλ.	$\frac{\delta\lambda}{H} \times 10^2$
			1800	9	0·50
			2300	10	0·44
			3000	13	0·43
			3300	15	0·45
			4200	20	0·48
			5100	24	0·47
			5700	25	0·44
			6300	28	0·44
			6700	28	0·42
			7600	32	0·42
9900	−47	−0·48	9900	43	0·43
			12700	55	0·43
			14600	66	0·45
16600	−82	−0·49	16600	76	0·46
			20800	94	0·45
			21400	97	0·45
			23400	106	0·45
24500	−115	−0·47	24500	112	0·46
30000	−149	−0·50	30000	137	0·46

s-components.

− side (outer).			− side (inner).			+ side (inner).			+ side (outer).		
H.	δλ.	$\frac{\delta\lambda}{H} \times 10^2$	H.	δλ.	$\frac{\delta\lambda}{H} \times 10^2$	H.	δλ.	$\frac{\delta\lambda}{H} \times 10^2$	H.	δλ.	$\frac{\delta\lambda}{H} \times 10^2$
						1300	24	(1·85?)	1800	43	2·40
			3300	−38	−1·15				3300	76	2·30
4300	−79	−1·84	5000	−62	−1·24	4000	57	1·43	4300	94	2·19
			5800	−74	−1·27	4300	62	1·41	5100	108	2·12
			6500	−78	−1·20	5100		1·33	5700	119	2·09
7000	−130	−1·86	7000	−83	−1·18						
7300	−136	−1·86	10200	−124	−1·21	16700	222	1·33	10200	199	1·95
			14300	−175	−1·22				10800	216	2·00
14200	−258	−1·82	16700	−206	−1·23	21500	292	1·36	18200	349	1·91
18550	−343	−1·85	18200	−224	−1·23	23000	313	1·36	19000	363	1·92
			20500	−255	−1·24				20600	399	1·94
			23000	−287	−1·25				21300	416	1·96

(+ 108)		
p-component.		
H.	δλ.	$\frac{\delta\lambda}{H} \times 10^2$.
2300	1	0
2900	2	0
3300	2	0
5700	−1	0
6700	0	0

(+ 185)					
p-components.					
− side.			+ side.		
H.	δλ.	$\frac{\delta\lambda}{H} \times 10^2$.	H.	δλ.	$\frac{\delta\lambda}{H} \times 10^2$.
2900	−20	0·69	2900	18	0·64
5100	−34	0·67	16600	88	0·53
7600	−52	0·68	21400	112	0·52
9900	−66	0·67	23400	124	0·53
12700	−85	0·67			
14200	−96	0·68			

II.—COMPLEX DISPLACEMENTS.

(− 160)							
p-components.					*s*-components.		
− side.			+ side.		− side.		
H.	δλobs.	δλcalc.	H.	δλobs.	H.	δλobs.	δλcalc.
2900	−4	−6	1800	11	1300	−4	−3
3300	−9	−8	2900	23	1800	−6	−5
5700	−23	−23	5100	33	2300	−9	−8
6300	−29	−28	5600	33	3300	−17	−16
6700	−32	−32	6300	37	4300	−28	−25
			6700	40	9800	−93	−91
			9900	45	11400	−113	−112
			12700	32	14300	−152	−153
					16700	−185	−185

$(H^2 \times 10^{-6} = -1.40\delta\lambda.)$

$(H^2 \times 10^{-6} = -0.612\delta\lambda + 0.00486\delta\lambda^2.)$

(− 107)		
s-component.		
− side.		
H.	δλobs.	δλcalc.
1300	−4	−5
3300	−28	−27
5100	−57	−57
10200	−164	−164

$(H^2 \times 10^{-6} = -0.363\delta\lambda + 0.0017\delta\lambda^2.)$

(− 94)

p-components.				s-components.				
− side.		+ side.		− side.			+ side.	
H.	$\delta\lambda_{obs}$	H.	$\delta\lambda_{obs}$	H.	$\delta\lambda_{obs}$	$\delta\lambda_{calc}$	H.	$\delta\lambda_{obs}$
18000	+1	3400	17	1200	−2	−2	1800	21
23000	+2	4200	17	1800	−4	−4	4300	62
29000	−5	5700	17	2200	−5	−6	5600	103
33000	−8	6300	14	2800	−10	−10	7000	128
42000	−23	6700	13	4000	−22	−22		
		7500	8	5600	−40	−39		
				6500	−52	−52		
				10800	−128	−125		
				12300	−158	−155		

$(H^2 \times 10^{-6} = -0.72\lambda + 0.0015\lambda^2.)$

(+ 108)

s-components.			
− side.		+ side.	
H.	$\delta\lambda_{obs}$	H.	$\delta\lambda_{obs}$
1000	−8	1300	13
1300	−13	1800	27
1800	−22	3300	54
5100	−82	4300	76
7800	−128		

(+ 185)

s-components.		
+ side.		
H.	$\delta\lambda_{obs}$	$\delta\lambda_{calc}$
1300	5	3
1800	8	5
2300	7	8
2800	10	12
3300	17	17
5600	49	48

$(H^2 \times 10^{-6} = 0.655\lambda.)$

The simplest type of separation is observed in the satellite whose position in non-magnetic field is $+46$. The p-components consist of two branches, which are parallel to the principal lines P_{-1} and P_{+1}. One of the branches towards the red is much more pronounced than that on the violet side. The positive branch is especially bright, as it is always distinctly to be observed by the side of the principal line. The s-components consist of a quartet, parallel to the principals $P_{\pm 2}$, $P_{\pm 3}$, but the intensity is widely different according to the components. Those parallel to P_{+3} and P_{-2} are brighter than those parallel to P_{+2} and P_{-3}, while with the principal, $P_{\pm 2}$ are a little brighter than $P_{\pm 3}$; thus for one branch of the quartet of this satellite, the order of intensity is inverted. The linear relation of the displacement with the field strength seems to be nearly fulfilled up to very high fields.

The p-components of the satellite $+185$ are displaced parallel to the principal, but the lines are weak and can no more be followed beyond 23 kilogauss for the $+$branch, while the $-$branch is obliterated by the principal line P_{+1}. The s-components of this satellite show anomalous behaviour similar to the type already noticed with the p-component of the satellite -242 (-239 according to our new measurement) in the green line of mercury. Another anomaly lies in the smallness of the amount of separation for s-components in comparison with p-components.

The satellite -18 has a negative p-component which is displaced wider than P_{-1}; the positive branch is probably eclipsed by P_{+1}, so that it does not appear well defined on the photograms. A singular anomaly is presented by the s-components. The separation takes place proportional to the field strength in all the observed branches, but the amount is less for the positive than for the negative; one of the latter branches is parallel to P_{-3}, while the other is farther down; there is thus greater dissymmetry in the effect. One reason for the preponderance of the negative displacement is probably to be found in the fusion of the negative branches of the satellites -160, -110, and -94 with those of -18.

In the s-components of $+108$, two faint branches are to be traced; by combining them with the undisturbed line in the p-component, we notice that the separation is of a triplet type similar to the principals of the violet line 4047.

The magnetic force produces anomalous effect on p-components of the satellites -160 and -94: the negative branch is represented by a parabolic curve, so that the

displacement is nearly proportional to the square of the field ; it gradually fades away and disappears in fields of a few thousand gauss. The + branch is curved for both lines, the concavity being turned towards the — side ; they both approach the negative branch of — 18, to which the lines are finally immersed at H = 9000 gauss for — 94, and at H = 13000 gauss for — 160. This singular phenomenon of the ultimate fusion of lines was already observed in the satellite — 242 of the green line. Such behaviour has already been observed by Wali-Mohammad * on the satellites of cadmium and bismuth lines, and is probably characteristic of the Zeeman effect of the satellites. It is questionable, if we have to consider these two satellites as belonging to the principal line, or to — 18, in which they are finally immersed. The positive branches of the s-components of these satellites fade away in tolerably weak fields, but the negative branch takes an hyperbolic course, and approaches — 18, almost asymptotically. Two of the satellites, — 160 and — 94, are immersed in the upper, and — 107 in the lower negative branch of — 18. This behaviour is similar to those already observed for — 160 and — 94 in the p-components, and for — 242 in the green line of mercury. The difference in the behaviour is that, in the p-components, the fusion of lines takes place with a component whose displacement is not proportional to the square of the field in the initial stage of separation, while with the s-component the contrary is the case.

The anomaly above described is mostly confined to satellites which do not lie in the immediate neighbourhood of the principal line.

We have noticed that the farthest satellite — 242 in the green line shared this characteristic to a remarkable degree, while for 4359, the satellites lying at — 160, — 107, — 94, and + 185 from the principal, show a similar mode of anomalous displacements. The satellites in the vicinity of the principal line seem to be much affected by it, and are generally displaced proportional to the field, the course of the curve running in most cases parallel to the branches of the prncipal line.

The above fact is also borne out by the experiments of Gmelin †, and Lunelund ‡, on the outermost satellite + 224 of the yellow line λ 5790 of mercury, and of Wali-Mohammad §, on cadmium and bismuth lines. Among the

* Wali-Mohammad, Diss. Göttingen (1912) ; *Ann. der Phys.* xxxix. p. 225 (1912).
† Gmelin, Diss. Tübingen, p. 41 (1909).
‡ Lunelund, *Ann. d. Phys.* xxxiv. p. 505 (1911).
§ Wali-Mohammad, *loc. cit.*

last-mentioned lines, whose displacements are proportional to the square of the field strength in the initial state, may be mentioned $+58$ of the cadmium line $\lambda 4800$ for p- and s-components, and -103 of the bismuth line $\lambda 4722$ for s-components.

The comparison of the present experiment with the results of previous investigators is of little importance, since the anomalies here discussed were not noticed in most cases. Gehrcke * and v. Baeyer were the first to investigate the Zeeman effect of a satellite of $\lambda 4359$ in weak fields ; the same satellite was afterwards investigated by Lunelund, but as the upper limit of the field did not exceed 3500 gauss, the measurements did not bring out the principal features discussed in the present paper. The lines on both sides of $P_{\pm 3}$, which appear in strong fields according to Wendt †, are probably the branches of the satellites -18 and $+46$; the correspondence with our result is not exact.

In his theory of the Zeeman effect, Voigt ‡ has shown that for a simple coupling with an electron, the change of wavelength for the p-component of a satellite takes place at first proportionally to the square of the field, and then according to an hyperbolic law. The behaviour of some of the satellites of the line here investigated corresponds to this theory as already noticed. In addition to this, we meet with several similar cases in the s-components; this evidently calls for a new discussion of a system with another kind of coupling. It may, however, be objected that the study of the mercury lines $\lambda 5461$, $\lambda 4359$, and $\lambda 4047$ is limited to a triplet of the second subordinate series, so that other kinds of displacements may appear with other lines and with lines of other elements. But the results of different experimenters on satellites of other spectrum lines show that the types of anomalies are not numerous, so that we may arrive at a satisfactory explanation of the satellites and their connexion with the principal line, by following the reason based on the mutual action of vibrating electrons. By the study of the three lines above-mentioned, we can obtain abundant experimental data for testing the theory of the coupling of electrons in explaining the different behaviours of the satellites in magnetic fields.

Physical Institute, University of Tokyo,
        July 28th, 1914.

* Gehrcke and v. Baeyer, *Ver. d. Deutsch. Phys. Ges.* viii. p. 399 (1906).
    † Wendt, *Ann. d. Phys.* xxxvii. p. 535 (1912).
    ‡ Voigt, *Ann. d. Phys.* xlii. p. 815 (1913).

XXVIII. *The Magnetic Deflexion of the Recoil Stream from Radium A.* By H. P. WALMSLEY, *M.Sc., and* W. MAKOWER, *M.A., D.Sc.*[*]

THE deflexions suffered in an electric and a magnetic field by the recoil stream of radium B produced by the disintegration of radium A have been studied by Russ and Makower[†] and by Makower and Evans[‡]. It was shown that the atomic mass of radium B has approximately the value 214 predicted by radioactive theory, and that each particle in the recoil stream carries one positive charge. It is of importance to repeat these experiments with greater accuracy in order to determine the atomic mass of radium B, and it is also of interest to find out how nearly the velocity of the particles in the recoil stream is in agreement with that to be predicted from a simple application of the law of the conservation of momentum. Experiments on the magnetic deflexion of the recoil stream have been completed and will be described, but the investigation of the electric deflexion has unfortunately had to be postponed.

When an atom of mass M disintegrates and emits an α particle of mass m with a velocity v, the atom recoils with a velocity V given by the equation

$$(M-m)V = mv. \qquad \qquad (1)$$

If the recoil stream and the α rays pass through a magnetic field of strength H, the radii of curvature ρ_r and ρ_a are respectively $\dfrac{(M-m)V}{He}$ and $\dfrac{mv}{2He}$, since the recoil particles carry only one charge, whereas the α rays carry two. If, therefore, the recoil stream and the α rays pass through the same magnetic field, the radius of curvature of the former

Fig. 1.
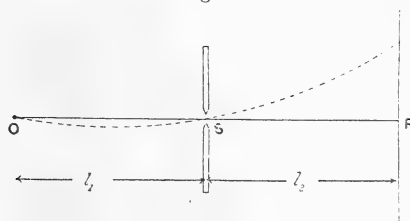
should be exactly double that of the latter. Using a line source O, a slit S, and a screen P placed perpendicular to the line OS (fig. 1), the particles passing through the magnetic

* Communicated by the Authors.
† Russ and Makower, Phil. Mag. Nov. 1910.
‡ Makower and Evans, Phil. Mag. Nov. 1910.

field will be bent into circles, and will strike the screen in lines parallel to the source and slit but displaced from the point P. If the distance $OS = l_1$ and the distance $SP = l_2$, then if the displacements d_α and d_r suffered by the α particles and recoil stream respectively are measured, the radii of curvature are given by the equations

$$\rho_a = \frac{1}{4d_a{}^2} \left\{ l_2{}^2 + d_a{}^2 \right\} \left\{ (l_1 + l_2)^2 + d_a{}^2 \right\} \left. \right\}$$

and

$$\rho_r = \frac{1}{4d_r{}^2} \left\} l_2{}^2 + d_r{}^2 \right\} \left\{ (l_1 + l_2)^2 + d_r{}^2 \right\} \left. \right\} , \quad . \quad . \quad (2)$$

whence $\dfrac{\rho_a}{\rho_r} = \dfrac{d_r}{d_a} \left\{ 1 + \dfrac{d_a{}^2 - d_r{}^2}{l_2{}^2} + \dfrac{d_a{}^2 - d_r{}^2}{(l_1 + l_2)^2} \right\}^{\frac{1}{2}}$ approximately.

$$. \quad . \quad . \quad . \quad (3)$$

If, therefore, the quantities d_α and d_r are measured, the radius of curvature of the recoil stream in the magnetic field can be compared with that of the α rays and the value of $\dfrac{(M - m)V}{e}$ for the recoil stream found without the necessity for an absolute determination of the value of the magnetic field or for measuring the quantities l_1 and l_2 with great accuracy, since these quantities occur only in small correcting terms.

The method depends upon the possibility of detecting the positions at which the α rays and recoil stream strike the screen P. This can be done easily in the case of α particles by using a photographic plate as the screen. Various plates were tried to see whether the recoil stream gives a developable image, but the tests, though not exhaustive, failed. It was found, however, that under suitable conditions, if the radium B was allowed to decay on the photographic plate *in situ*, a photographic image was obtained by the subsequent emission of α rays from the radium C formed from it.

The apparatus consisted of a stout brass box, the internal dimensions of which were 18 cm. × 3·7 cm. × 0·9 cm. (fig. 2). The box contained the slit S and the photographic plate P. It was closed at one end by means of a piece of plate glass A ground on to a broad flange and at the other by a closed ground joint B. To this was attached on the end of a brass rod C a plate which carried the active wire. The apparatus was evacuated through the vertical tube D, which was provided with another joint by means of which it could be detached from the rest of the apparatus when necessary. The slit S was horizontal and was 0·1 mm. wide. It was mounted

on a frame which could be adjusted in any position within the box; the photographic plate was also mounted on an adjustable carrier.

Fig. 2.
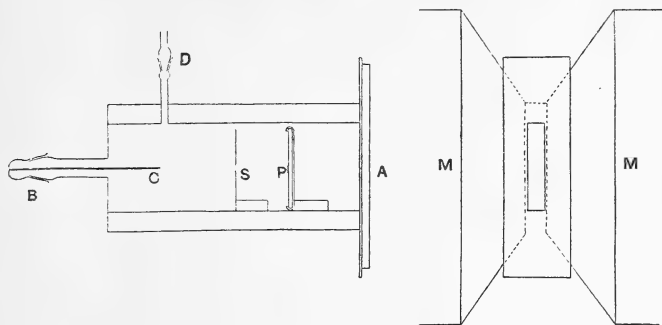
The box was placed between the pole-pieces M of a large electromagnet. The distance between the pole-pieces was 1 cm. and their face area 16 cm. × 5 cm. A current of 11 amperes gave a uniform field of about 15,000 gauss over the whole area, so that throughout their paths the α rays and recoil stream were in a uniformly strong magnetic field. The whole of the glass apparatus near to the box was painted black. The active source used consisted of radium A collected on a platinum wire 0·4 mm. in diameter. This fitted into a groove cut in the plate C. The groove was adjusted until it was horizontal and parallel to the slit S, and reference marks were then placed in white paint on the two parts of the joint B for simplicity in subsequent adjustments.

In order to insure a high efficiency of recoil, the wire was made active with radium A in an apparatus similar to that described by Wertenstein[*], in which the wire could be removed from the emanation without drawing it through mercury. From 50 to 100 millicuries of emanation were used, and the wire was exposed to the emanation for six minutes. At the end of the exposure the wire was dropped for a few seconds into a glass tube maintained at 400° C. to remove emanation. The wire was then fixed in position in the groove cut in the plate C (fig. 2) by means of a speck of soft wax. The stopper B was then replaced and rotated until the wire was horizontal and the magnetic field was excited. These operations usually occupied 2 to 3 minutes. The box was rapidly evacuated, first by means of a Fleuss-

[*] Thèses presentées à la Faculté des Sciences, Paris, 1913, p. 90.

oil-pump and then by the use of charcoal cooled in liquid air. Pressures were read on a McLeod gauge. The pressure gradually decreased during the experiment, but was usually of the order of 1/1000 mm. after the first three minutes. Three minutes after introducing the stopper B the field was reversed, and the photographic plate subjected to a further radiation for 9 to 12 minutes. At the end of the exposure the plate was removed and wrapped in black paper for a period of about three hours to allow the active deposit to decay. It was then developed in the usual way. The plate used was a piece of Ilford Process plate 3·3 cm. × 0·8 cm., which was sufficiently large to prevent the film becoming detached during development. The activity of the wire was also measured. Its γ-ray activity at the maximum usually corresponded to about one milligram of radium C.

The best arrangement of wire, slit and plate is not easy to foresee. From equation (3) it is evident that the accuracy obtained for the ratio $\frac{\rho_a}{\rho_r}$ depends upon the accuracy with which the distances d_a and d_r can be measured. These quantities increase in the first place with the strength of the magnetic field, which was made as intense as practicable without over-heating the magnet. The accuracy with which the ratio $\frac{\rho_a}{\rho_r}$ can be measured depends also on the width of the images relative to their distance apart. The width of the image can be reduced to a certain extent by employing a narrow slit and a narrow source, but the amount of active matter which reached the plate is rapidly reduced by the use of fine slits, and it is impossible to collect enough radium A on a very fine wire. In practice we obtained very satisfactory results by using as source a platinum wire of diameter 0·4 mm. and a slit 0·1 mm. wide. The distance l_1 was kept permanently 3·0 cm., the slit carrier being held in position by metal stops. When l_2 was 1·84 cm. we obtained a dense image easily measurable, but the maximum value of d_a obtained was only 2 mm. With $l_2 = 2·85$ cm. the image was just measurable in the case of the recoil lines, and d_a increased to 3·7 mm.; but with $l_2 = 3·5$ cm. using the same amount of active material, the recoil image though just visible was quite unmeasurable. In all cases the α-ray images were remarkably sharp and distinct. This rapid reduction in the intensity of the recoil images is rather striking, and explains many failures in previous experiments.

In fig. 1, Pl. V., is given a reproduction of one of the

photographs taken which is not without interest. The α-ray lines show structure, the image being denser at the edges than at the centre. This is clearly brought out when the line is examined under a low-power microscope. From the manner in which the recoil images were obtained, it was not to be expected that they would show any characteristic structure. They were generally diffuse, and even in the case of the strongest lines there was not a vast difference between their density and that of the background of the photographic plate, which was always slightly fogged by the β and γ ray radiation from the active deposit. In one case it was noticed that the centre corresponding to the recoil lines was displaced relatively to that corresponding to the α-ray lines, *i. e.* one recoil line appeared to be nearer its α-ray line than the other. This was apparently due to a difference in the efficiency of recoil from different parts of the circumference of the wire which displaced the position of maximum density within the lines. The ratio of the distance between the α-ray lines to that between the recoil lines is, however, unaltered by this dissymmetry. A second fairly strong line was often found near to the α-ray line obtained after reversing the field. This was due to the α particles from the radium C which had grown on the wire during the experiment. In many cases this radium C line was stronger than the recoil line, and occasionally a faint radium C line was also visible near the initial radium A line. A direct comparison of the velocities of the α particles from radium A and radium C can be made by this method[*], and thus the empirical relation between the range and velocity of α particles given by Geiger can be tested for this case[†].

In measuring the photographic plates, the distances between the centres of the lines were determined. Each photographic plate was mounted in a frame of black paper so as to expose only the essential part of the photograph and mounted in a clamp at a distance of about a metre from a travelling telescope of low magnifying power. To illuminate the plate an electric lamp was placed behind a sheet of opal glass and connected in series with an adjustable resistance. It was found that by adjusting the intensity of illumination of the plate, the contrast between the clear portions of the plate and the faint recoil lines could be best brought out at a certain intensity of illumination. Although the recoil lines were considerably broader than the fiducial line in the eyepiece of the telescope, yet when this was set on the image it was practically impossible to see the recoil line on account

[*] Tunstall and Makower, *infrà*, p. 259.
[†] Geiger, Proc. Roy. Soc. A. lxxxiii. p. 505 (1910).

of its faintness. This difficulty was overcome by arranging that the fiducial line should cover only one half of the length of the image. Some bias in making the settings was inevitable, and it seemed impossible to increase the accuracy of the readings beyond a certain limit by multiplying observations. This was due to a tendency to adjust the fiducial line on marks and dust spots which though faint occurred on the plates. We eliminated this as far as possible by inverting the photographic plate at intervals, thereby changing its appearance in this respect, and by using the independent measurements of three observers. Throughout we have assumed that the densest part of the image in the case of the recoil lines was the centre. The magnification used was controlled by the intensity of the recoil lines; the greater their density, the greater was the magnification that could be employed. Although the recoil lines were distinctly visible to the naked eye on each plate taken, yet only about half the plates could be used for making accurate measurements.

The measurements were made in sets of ten and the plate was always readjusted between each set, so as to use different parts of the divided scale of the travelling telescope. About six sets were taken on each plate. The final values of the ratio d_r/d_a for each plate given in the table are the means of all the observations. The vernier readings were taken to the nearest hundredth of a millimetre, but the means were worked out to the next significant figure. The results of the measurements on several plates are given in the following table, an inspection of which shows that the radius of curvature of the recoil stream in a magnetic field is double that of the α rays with a high degree of accuracy.

TABLE.

No. of plate.	Approximate field in gauss.	l_1 in cm.	l_2. in cm.	$\dfrac{d_r}{d_a}$.	$\dfrac{\rho_a}{\rho_r}$.
1.........	13700	3·5	1·84	0·4934	0·4959
2.........	14500	3·5	2·85	0·4977	0·5017
3.........	15000	3·5	1·84	0·4981	0·5008
4.........	14600	3·5	2·85	0·4967	0·5006
5.........	15000	3·5	1·84	0·5006	0·5055
				Mean ...	0·5009

We are greatly indebted to Mr. N. Tunstall for his assistance in measuring the plates. With his valuable help we have been able to increase the accuracy of the experiment by using the results of three independent observers.

XXIX. *The Velocity of the α Particles from Radium A.*
By N. Tunstall *and* W. Makower [*].

[Plate V. fig. 2.]

THE velocity of the α particles from radium C has
recently been very accurately determined by Ruther-
ford and Robinson[†]. The value given is $1\cdot922 \times 10^9$ cm.
per second, and from this number the velocities of the
α particles from other radioactive substances are calculated
by Geiger's formula

$$v^3 = k\mathrm{R},$$

which gives the relation between the velocity v of an
α particle and its range R in air. The quantity k is a
constant.

A direct comparison of the velocity of the α particles from
radium A with that of the particles from radium C, does not
appear as yet to have been made ; and as the apparatus
used to measure the magnetic deflexion of the recoil stream
from radium A [‡] was also suitable for this purpose, ex-
periments were made to determine the ratio of the velocities
of the α particles from radium A and radium C as accurately
as possible.

The apparatus used was the same as that used by
Walmsley and Makower [§]. The wire O (fig. 1, p. 253) was
made active by exposure for eight minutes to radium emana-
tion and quickly mounted in the apparatus, which was then
evacuated as rapidly as possible. The α rays passing
through the slit fell on the photographic plate, which
was subsequently developed. A field of about 14,000 gauss
was applied between the pole-pieces of the magnet. The
α rays from the radium A on the wire thus fell on the
photographic plate, producing an image of the slit. After
four minutes the field was reversed for fifteen minutes,
and a second image due to the α rays from radium A was
obtained. During the interval which had elapsed since the
exposure of the wire to the emanation, sufficient radium C
had grown on the wire to produce simultaneously on the
photographic plate a second and slightly less deflected
image. By this time all the radium A on the wire had
decayed, and the field was again reversed for ten minutes
so as to obtain an image from the α rays from radium C on

* Communicated by the Authors.
† Rutherford and Robinson, Phil. Mag. Oct. 1914, p. 522.
‡ Walmsley and Makower, Phil. Mag. *suprà*, p. 253.
§ *Loc. cit.*

the same side of the centre of the plate as the first image of radium A. The plate was then removed and developed, and showed two pairs of lines due respectively to the α rays from radium A and radium C. The appearance of the plate can be seen from fig. 2 (Pl. V.). The plates were examined by means of a travelling telescope, and the distances, d_A and d_C, between the two lines due to radium A and those due to radium C were measured in the way described for determining the deflexion of the recoil stream *. From these measurements the ratio of the radius of curvature of the α rays from radium A to that for the rays from radium C could easily be calculated. The results obtained are given in Table I., in which the numbers recorded for each plate represent the mean of thirty observations. In each experiment the distance from the wire to the slit was 3·6 cm. In the case of plate 1 the distance from the slit to the photographic plate was 3·60 cm., and for each of the other plates this distance was 2·85 cm. The small variations in the deflexions on plates 2, 3, and 4 were due to differences in the strengths of the magnetic fields used.

<div align="center">TABLE I.</div>

Plate.	Distance in cm. between Radium A lines. d_A.	Distance in cm. between Radium C lines. d_C.	$\dfrac{d_A}{d_C}$.	Ratio of radii of curvature.
1.	1·0548	·9238	·8757	·8784
2.	·7831	·6359	·8759	·8782
3.	·7334	·6437	·8778	·8796
4.	·7376	·6480	·8782	·8805
			Mean	·8792

Taking the velocity of the α particles from radium C as $1·922 \times 10^9$ centimetres per second, this gives for the velocity of the α rays from radium A the value $1·690 \times 10^9$ centimetres per second, which is in close agreement with the value $1·693 \times 10^9$ centimetres per second calculated by Geiger's formula from the known ranges of the α particles.

<div align="center">* *Loc. cit.*</div>

XXX. *Frictional Electricity on Insulators and Metals.* *By*
W. Morris Jones, *B.Sc., Research Student of the University
of Wales* *.

IN a recent paper Morris Owen † describes a series of
experiments, in which he obtained absolute measure-
ments of the charges produced on solid bodies by known
amounts of frictional work. In particular, he rubbed
ebonite and glass with slate and copper under various con-
ditions as to pressure, and found that with a sufficient
amount of frictional work the charges reached a constant
maximum, and that this maximum was independent of the
pressure applied during the rubbing, but was reached with a
smaller quantity of work the greater the pressure.

As there seems to be but little known about frictional
electricity, the investigations described below were under-
taken with the object of discovering new facts which might
be of assistance in forming a quantitative theory. In these
experiments, after the method adopted by Owen, measure-
ments were made of the charge produced on a surface by
friction and of the frictional work spent in generating it.
Apart from any theory of the phenomenon, this seems
the most convenient way of stating the results of the
experiments.

Apparatus.

The apparatus employed was essentially the same as that
used by Owen, but there were several improvements. The
rubbing apparatus consisted of a slate wheel round the rim
of which rubbers of various soft materials were placed. The
wheel, of moderate moment of inertia and ·8 cm. thick,
turned in bearings fixed in a wooden framework, and could
be set into rotation by a known weight falling through a
measured height. The weight was attached to a cord passing
over a light pulley in the ceiling and wound round a wooden
drum fixed on the wheel. A vertical pole graduated up-
wards in decimetres gave the distance through which the
weight fell. In later stages of the work the wheel was
driven by an electric motor of variable speed.

The specimens rubbed were usually disks about 1·2 cm.
in diameter, and were of various insulating and metallic
materials. They were mounted with an insulating cement on

* Communicated by Prof. E. Taylor Jones.
† Phil. Mag. xvii. p. 457 (1909).

small **T**-shaped strips of ebonite, which could be firmly fixed
to an ebonite holder, fig. 1.   The holder was made of two
pieces of ebonite connected across by a block of well insu-
lating amber, and could be fitted into a bayonet-socket

Fig. 1.
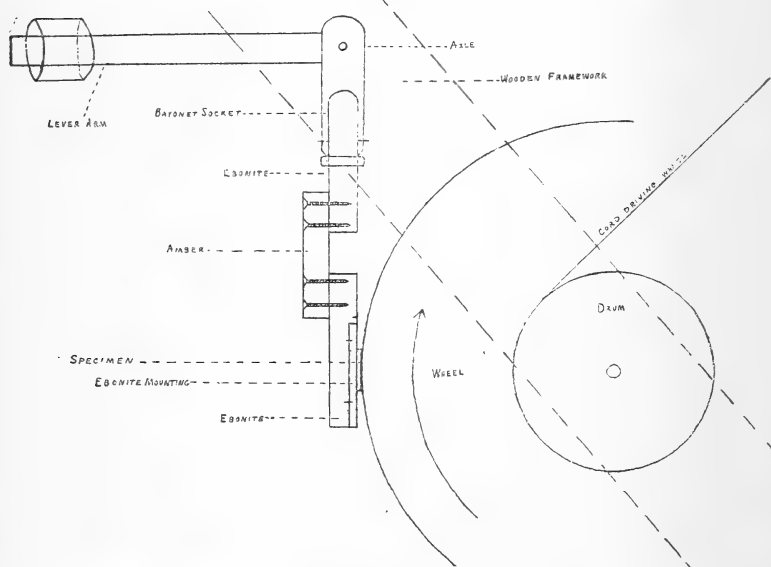
forming one arm of a lever bent at right angles.   The lever
turned about an axle fixed in the wooden framework sup-
porting the wheel, so that, when the holder was in position,
this arm of the lever was vertical with the specimen pressing
horizontally against the rubber, the thrust between the
specimen and the rubber being produced by a lead weight
placed in any suitable position on the other lever-arm.   A
rub was effected by releasing the wheel, which was then set
rotating by the falling weight, the specimen being separated
from the rubber just before the wheel came to rest.   Know-
ing the time of fall of the weight, the kinetic energy lost on
impact of the weight with the floor could be taken into
account in the calculation giving the work spent against the
friction of the specimen on the rubber.   The amount of
energy lost at the bearings of the wheel was small and could
be neglected.
     Immediately after a specimen was rubbed, the holder
supporting it was quickly withdrawn from the socket and

suspended by a string over a deep metal jar into which the specimen could be lowered. The jar was placed inside, and insulated by quartz supports from, a larger earth-connected jar, which served to increase the capacity and to shield the inner jar from outside influences. The inner jar was connected by a fine wire passing through sulphur plugs in the outer, to the upper plate of a parallel plate condenser, and also to one of the terminals of a quadrant-electrometer, the lower plate of the condenser and the other terminal of the electrometer being permanently earthed. The deflexions of the needle were observed by a telescope and illuminated scale. The zero of the scale was obtained by earthing the terminal of the electrometer by means of a suitable mercury-cup key operated by a string. The whole measuring system was enclosed in a wooden box with a window for the electrometer, the inside of the box being covered with tinfoil and earthed. The box served to shield the whole apparatus from external influences and by means of drying agents inside it kept the apparatus perfectly dry. The needle of the electrometer was suspended by a platinum wire ·01 mm. in diameter, and throughout the experiments was maintained at a potential of 100 volts by a small battery of Weston cells.

In measuring the charge on a specimen after a rub, the zero of the electrometer was first observed, the earth connexion removed, and the specimen lowered into the jar and the deflexion noted.

The insulation of the apparatus was frequently tested, and the holder cleaned with a warm cloth, so that the specimen should lose no appreciable charge during its removal from the lever to the jar. Provided the holder were clean and dry, no appreciable change in deflexion was noticed, even when the charged specimen was replaced in the socket and then again removed and lowered into the jar. Good insulation of the specimen was thus secured by the use of amber as a connecting piece in the holder, and the upper piece of ebonite could be freely handled when being placed into or withdrawn from the socket without any leakage of charge from the specimen.

Before each rub the specimen, holder, and rubber were completely discharged by exposure to radiations from radium.

Preliminary experiments showed that it was necessary to reduce considerably the sensitiveness of the electrometer owing to the large values of the charges produced on some of the specimens. This was done by shortening the suspending wire, so that the needle could still be maintained throughout the experiments at a potential much higher than

that of the insulated quadrants, without unduly increasing the deflexion.

The scale was calibrated by the difference of potential due to a known current passing through a known variable resistance. The capacity of the measuring system was determined by the method of mixtures, using a standard condenser. Knowing the capacity of the electrometer and accessories, and also knowing the potential of the insulated quadrants corresponding to any deflexion of the needle, the charge producing that deflexion was obtained.

The Insulators.

In rubbing the specimens, care was taken to bring the middle part of the specimen evenly into contact with the rim of the rubbing wheel. If this was not done, the deflexion obtained with insulators was always too small owing to the smaller area of contact. This precaution also prevented the sliding contact from breaking into a series of impacts. It was also found necessary to give the insulators a rest after each rub, for if an insulator was rubbed a number of times in succession the deflexions rose to the maximum, though the work done was the same for each rub and less than that required to give the maximum for a first rub. Owen also observed this effect, and found that he had to give his specimens a rest of about three hours after each rub with slate or copper. In the experiments described here, the rest needed was far shorter, this being apparently due to the fact that the rubbers used were softer. To get the rubber as soft as possible a few layers of the material were wound round the wheel.

The insulators rubbed were fused quartz disks, quartz crystal, glass, polished ebonite, amber, sealing-wax, and crystals of fluorspar, Iceland spar, and heavy spar. The rubbers were bands of flannel, silk, and chamois leather wound round the rim of the wheel, the axle of which was earthed, and the normal thrust between specimens and rubbers was in all cases 178 grams weight.

The following tables give the charges in electrostatic units produced by various quantities of frictional work represented in joules, when four typical specimens were rubbed with flannel, silk, and leather.

TABLE I.

Fused Quartz.

Positive electricity on the quartz when rubbed with flannel, silk, and chamois leather.

Diameter of specimen 1·2 cm.

Frictional work in joules.	Charge in E.S.U. when rubbed with		
	Flannel.	Silk.	Leather.
·4885	8·827	4·094	2·518
·9771	9·447	5·038	3·149
1·4655	10·077	5·983	3·779
1·9540	10·392	6·928	4·094
2·4425	10·581	7·558	4·409
3·4195	10·800	8·187	5·353
4·3965	10·917	8·817	5·668
5·8620	10·862	9·132	6·298
7·8160	10·916	9·447	6·928
9·7710	10·958	9·636	7·118
12·2125	10·946	9·747	7·492
14·6550	10·950	9·761	7·557

TABLE II.

Glass.

Positive electricity on glass when rubbed with flannel, silk, and chamois leather.

Diameter of specimen 1·2 cm.

Frictional work in joules.	Charge in E.S.U. when rubbed with		
	Flannel.	Silk.	Leather.
·4885	2·519	1·260	·315
·9771	3·464	3·169	·629
1·4655	4·094	4·724	·819
1·9540	4·724	6·298	·945
2·4425	5·241	7·085	1·070
3·4195	6·241	7·557	1·260
4·3965	6·613	8·975	1·575
5·8620	6·928	9·888	1·732
7·8160	7·873	10·328	1·889
9·7710	8·819	10·643	2·078
12·2125	8·820	10·738	2·204
14·6550	8·818	10·725	2·212

TABLE III.

Ebonite.

Negative electricity on ebonite when rubbed with flannel, silk, and chamois leather.

Diameter of specimen 1·2 cm.

Frictional work in joules.	Charge in E.S.U. when rubbed with		
	Flannel.	Silk.	Leather.
·4885	5·983	2·834	1·575
·9771	7·558	4·409	2·519
1·4655	8·187	5·668	3·401
1·9540	8·502	6·298	3·621
2·4425	8·943	6·613	3·968
3·4195	9·762	7·090	4·031
4·3965	10·077	7·206	4·220
5·8620	10·549	7·558	4·245
7·8160	10·833	7·778	4·219
9·7710	10·991	7·841	4·220
12·2125	11·085	7·868	4·346
14·6550	11·022	7·872	4·250

TABLE IV.

Amber.

Negative electricity on amber when rubbed with flannel, silk, and chamois leather.

Diameter of specimen 1·2 cm.

Frictional work in joules.	Change in E.S.U. when rubbed with		
	Flannel.	Silk.	Leather.
·4885	6·928	3·905	2·204
·9771	8·439	4·724	2·992
1·4655	8·502	5·479	3·464
1·9540	8·817	5·983	3·779
2·4425	9·132	6·298	3·887
3·4195	9·321	6·487	4·094
4·3965	9·193	6·613	4·283
5·8620	9·257	6·718	4·314
7·8160	9·233	6·739	4·345
9·7710	9·238	6·723	4·392
12·2125	9·269	6·738	4·440
14·6550	9·269	6·770	4·409

In figs. 2 and 3 the charges produced by various amounts
of work are plotted as curves. They show, as observed by

Fig. 2.

CHARGE IN ELECTROSTATIC UNITS

QUARTZ & FLANNEL (+)

QUARTZ & SILK (+)

QUARTZ & LEATHER (+)

FRICTIONAL WORK IN MILLIONS OF ERGS

Fig.

CHARGE IN ELECTROSTATIC UNITS

EBONITE & FLANNEL (—)

GLASS & SILK (+)

AMBER & FLANNEL (—)

GLASS & FLANNEL (+)

EBONITE & SILK (—)

AMBER & SILK (—)

AMBER & LEATHER (—)

EBONITE & LEATHER (—)

GLASS & LEATHER (+)

FRICTIONAL WORK IN MILLIONS OF ERGS
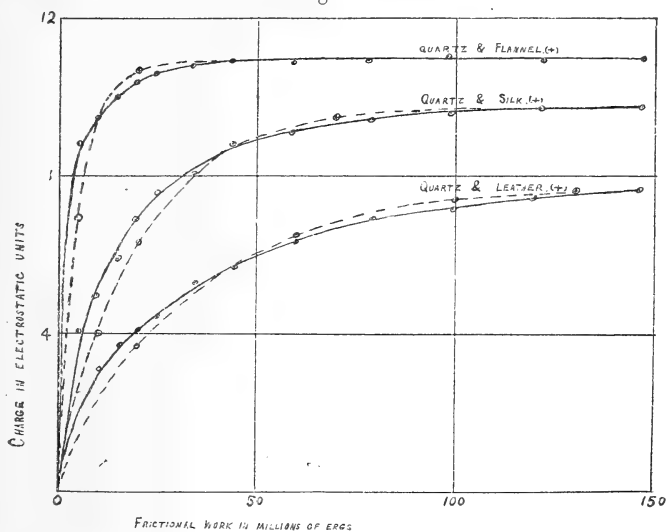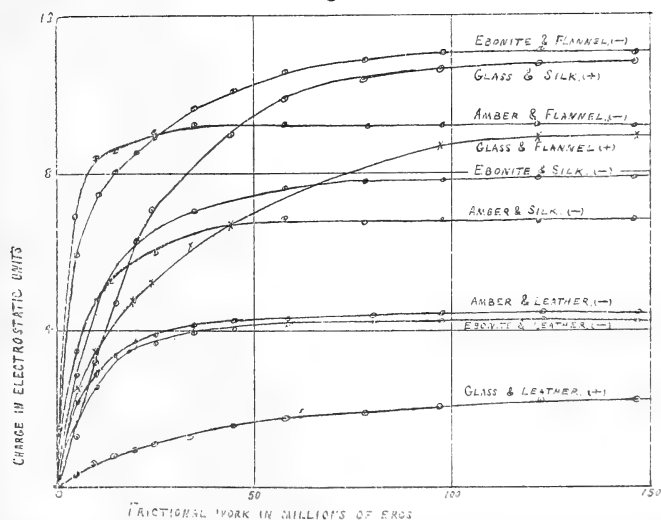
Péclet * and Owen †, that with a sufficient amount of work,
the charges reach a constant maximum. Results have been

* *Ann. de Chimie et de Physique*, lvii. p. 337 (1834).
† *Loc. cit.*

obtained for the other materials rubbed and have been plotted as curves, which show a similar form.

<div align="center">TABLE V.</div>

Specimen.	Maximum charge in E.S.U. when rubbed with		
	Flannel.	Silk.	Chamois leather
Quartz	10·950 (+)	9·761 (+)	7·557 (+)
Glass....................	8·818 (+)	10·725 (+)	2·212 (+)
Fluorspar	7·085 (+)	11·596 (+)	1·260 (+)
Iceland spar.........	8·817 (+)	11·818 (+)	1·236 (+)
Heavy spar	4·151 (+)	11·521 (+)	·945 (+)
Ebonite...............	11·022 (−)	7·872 (−)	4·250 (−)
Amber	10·707 (−)	7·870 (−)	4·726 (−)
Sealing-wax	9·269 (−)	6·770 (−)	4·409 (−)

Table V. gives the values in electrostatic units of the maximum charges produced on the insulators by friction with the rubbers. It is interesting to note that the transparent insulators were positively charged when rubbed with the three materials, and that the opaque substances all became negatively charged.

The maximum charges produced by friction with flannel, silk, and chamois leather are much greater than those obtained by Owen, whose specimens, however, were rubbed with hard materials, viz. slate and copper. This is probably due to the different nature and hardness of the rubbing surfaces. The soft rubbers used in the present experiments allowed a larger area of the specimen to come into contact with the rubber. It is also possible that a hard rubbing surface cuts up or wears away the surface of the specimen.

<div align="center">*Metallic Specimens.*</div>

In the experiments with the metals, the rubber had to be a good insulator and thoroughly dry, otherwise the charge generated leaked away through the rubber to earth as fast as it was produced. For this reason the metallic specimens were rubbed only with silk bands. The insulation of the silk was frequently tested by bringing the cap of a charged electroscope into contact with the band when on the wheel, and observing the rate at which the leaves collapsed. Owing to the hygroscopic nature of the silk, the material had to be kept warm and dry by placing a stove underneath the wheel. The insulation was further improved by having a band of indiarubber between the silk and the slate.

In rubbing the metals, reversals of the sign of electrification were frequent, and appeared to be due to several

causes. If the surface of the metal had become tarnished by oxide, the charge generated was low and in some cases reversed in sign. This reversal was noticed in the case of zinc and iron. If the surfaces of these metals were rubbed when tarnished, the charge was positive for moderate amounts of rubbing and negative for greater amounts, whereas the surfaces when previously cleaned with fine emery-paper always showed a negative charge. Apparently the rubbing gradually wore off the film of oxide and ultimately produced a charge similar to that obtained on the pure metal. A reversal of the sign of electrification also appeared when the silk rubber had been used for some time, and was probably due to the silk having become smeared with oxide. A fresh silk band always gave an electrification of the proper sign when the cleaned specimens were rubbed.

When the metals were all cleaned with very fine emery-paper, all the specimens except thallium, lead, and bismuth (which have the highest atomic weight) gave a negative charge at the first rub. Continued rubbing, however, produced a polish on the metals, and then it was found that the negative charges on aluminium, iron, copper, zinc, and antimony became less and less and changed to positive, though the other metals, on continued rubbing, did not show this effect.

Owing to these reversals and to the difficulty of preventing a roughened surface becoming smoothed out and polished by the friction, the specimens were, as far as possible, finally tested all with their surfaces at about the same degree of polish and with fresh silk bands.

The metals rubbed were lithium, boron, aluminium, calcium, iron, copper, zinc, silver, tin, antimony, platinum, gold, thallium, lead, and bismuth. The metals which could be obtained in the form of thin disks 1·2 cm. in diameter were soldered on brass cylinders 3 mm. thick, and second specimens were in some cases cemented on ebonite cylinders of the same thickness. Metals such as iron were made up to the same dimensions as the brass cylinders. All the above metals were rubbed for a maximum charge, and measurements of the charges produced by various amounts of work were also taken for a few typical specimens. In the case of the metals that readily tarnish in air, a few rubs were rapidly given immediately after cleaning their surfaces. The boron, supplied amorphous, had to be made up into a thick paste and allowed to set hard before it could be tested. Some of the specimens employed were of the ordinary commercial grade of purity, those of the rarer metals being refined.

Fig. 4 shows the curves for some of the metals. In shape they are, as might be expected, very similar to those of the insulators. The maximum charge is, however, greater on some of the metals than on any of the insulators.

Fig. 4.
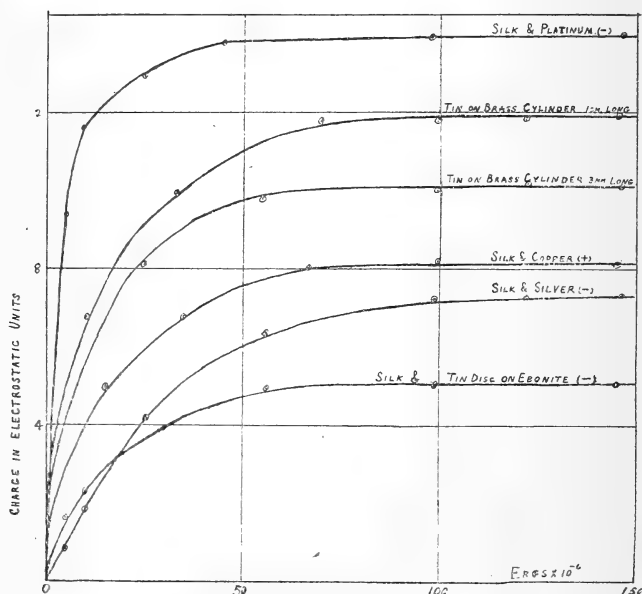
With the metals, capacity plays an important part in the value of the maximum charge generated. Three tin disks 1·2 cm. in diameter were mounted, one on ebonite and the other two on brass cylinders 3 mm. and 1 cm. thick. On being rubbed, the specimen mounted on the longer metal cylinder gave the greatest maximum charge, and the disk on ebonite gave the least, while the specimen on the short metal cylinder gave a charge of intermediate value. The three results in this case are shown in fig. 4. Apparently, therefore, the charge generated on a metallic specimen by a given amount of work increases with the capacity of the specimen.

The following classification of the metals according to the sign of the charge, shows that the metals examined can be divided into three groups :—

Au ⎫ Negatively charged
Pt ⎪ when rubbed
Sn ⎰ with silk.
Ag ⎭

Sb ⎫ Positively charged if
Zn ⎪ polished, negatively
Cu ⎬ charged if rough,
Fe ⎪ when rubbed with
Al ⎭ silk.

Bi ⎫ Positively charged
Pb ⎬ when rubbed
Tl ⎭ with silk.

The sign and magnitude of the charge produced by the friction of the metals do not appear to be a well-defined physical property of the metals. A possible relation between the maximum charges for different elements would thus be difficult to obtain, since, except with metals of high atomic weight, the sign of the charge seems to be largely determined by the physical state of the surface, and not merely by the nature of the material rubbed. Iu fig. 5 the maximum

Fig. 5.
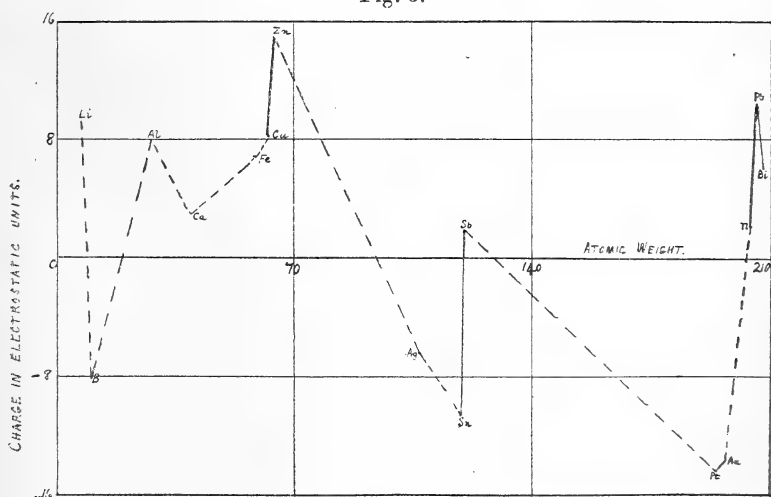
charge obtained by the friction of the surfaces of the metal, polished when possible, is plotted against the atomic weight. An examination of the curve shows that there appears to be here some evidence of a periodicity in property with increase of atomic weight, and that, like some other physical properties of the elements, this property possibly conforms to the Periodic Law.

Additional Experiments.

Some of the insulators and metals were rubbed in strong magnetic and electric fields, but no change in the maximum charge produced was noticed. The influence of temperature on the maximum charge was also investigated, and in this case also no effect was observed. In some experiments the rubbing wheel was driven by a motor, and the influence of pressure between rubber and specimen and that of velocity of the rubbing surface were investigated. From the results obtained, it appears that the maximum charge is independent of the pressure and of the velocity*.

General Conclusions.

It has often been supposed that frictional electricity is of the nature of contact electricity, the frictional work being expended in bringing the surfaces into closer contact†. It should, however, be noted that in Owen's experiments, mere contact without rubbing did not in any case produce the slightest evidence of charge on his specimens, and the same result was found in the course of the present experiments. Frictional electricity appears, therefore, to be an effect of a different order from that of contact electricity, and it is worth while considering whether the facts cannot be accounted for on some other hypothesis.

Let us assume that the rubbing friction has the effect of removing electrons from either the rubber or the specimen at a rate proportional to the rate of working. Then if e is the total quantity of electricity liberated by a quantity of work w, we may write

$$\frac{de}{dt} = a\frac{dw}{dt}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where a is a factor depending on the nature of the materials and also upon the normal thrust between the bodies; a is a constant during any one experiment.

We now assume that during a rub, leakage of electricity takes place at a rate proportional to the total charge present, Q, and to the rate at which fresh surface of the rubber is coming into contact with the surface of the specimen, the total leakage being e'. The velocity of the rubber is proportional to the rate of working, so that this law of leakage

* This result was stated by Péclet.
† Helmholtz, *Wissenschaftliche Abhandlungen*, Erster Band, p. 860.

may be written

$$\frac{de'}{dt} = b \cdot \frac{dw}{dt} \cdot Q, \quad \ldots \quad \ldots \quad (2)$$

where b is also a constant. The total charge existing on the specimen will now be

$$Q = e - e'. \quad \ldots \quad \ldots \quad (3)$$

From these equations we find

$$\frac{dQ}{a - bQ} = dw,$$

which, on being integrated, gives

$$Q = \frac{a}{b}(1 - \epsilon^{-bw}), \quad \ldots \quad \ldots \quad (4)$$

the constant of integration being determined by the fact that Q and w vanish together.

On this theory the frictional electricity reaches a constant maximum value, $\frac{a}{b}$, when the generation of charge is compensated by the leakage.

The constants, a/b and b, of (4) can be determined for any particular case from two points on the experimental curve, and Q can hence be calculated for any value of w. As a rule, the theoretical curves so obtained show fair agreement with the experimental curves, the chief difference being that the calculated curve is generally rather steeper in the middle part of the curve. Curves calculated in this way are shown in broken lines in fig. 2, for quartz when rubbed by flannel, silk, and leather.

In order to account for the result that the maximum charge is independent of the pressure, it is necessary to suppose that a and b contain as factors the same function of the pressure. In the case of the metallic specimens, where $Q = CV$, if C is the capacity and V the potential of the specimen, the leakage in equation (2) should be assumed to be proportional to V; in other words, the coefficient b is inversely proportional to the capacity. It follows by equation (4) that, in the case of two specimens of the same material but of different capacities, the maximum charge should be greater for the specimen of greater capacity, and that the slope of the rising portion of the curve should be steeper for this specimen. Less work should be necessary, therefore, to produce any given charge in the case of the

specimen of greater capacity. These results agree with the facts as indicated by the curves of fig. 4.

It seems probable, therefore, that a satisfactory theory of frictional electricity can be formed on the lines indicated, though in the form given above the theory is doubtless far from perfect.

In conclusion, I desire to express my best thanks to Professor E. Taylor Jones for much valuable help and advice during the course of the work.

Physics Laboratory,
University College of N. Wales, Bangor,
October 1914.

XXXI. *On the Widening of Spectrum Lines.* *By* Lord RAYLEIGH, *O.M., F.R.S.*[*]

MODERN improvements in optical methods lend additional interest to an examination of the causes which interfere with the absolute homogeneity of spectrum lines. So far as we know these may be considered under five heads, and it appears probable that the list is exhaustive :—

(i.) The translatory motion of the radiating particles in the line of sight, operating in accordance with Doppler's principle.

(ii.) A possible effect of the rotation of the particles.

(iii.) Disturbance depending on collision with other particles either of the same or of another kind.

(iv.) Gradual dying down of the luminous vibrations as energy is radiated away.

(v.) Complications arising from the multiplicity of sources in the line of sight. Thus if the light from a flame be observed through a similar one, the increase of illumination near the centre of the spectrum line is not so great as towards the edges, in accordance with the principles laid down by Stewart and Kirchhoff ; and the line is effectively widened. It will be seen that this cause of widening cannot act alone, but merely aggravates the effect of other causes.

There is reason to think that in many cases, especially when vapours in a highly rarefied condition are excited electrically, the first cause is the more important. It was first considered by Lippich [†] and somewhat later independently by myself [‡]. Subsequently, in reply to Ebert,

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[*] Communicated by the Author.
[†] Pogg. *Ann.* t. cxxxix. p. 465 (1870).
[‡] 'Nature,' vol. viii. p. 474 (1873) ; Scientific Papers, vol. i. p. 183.

who claimed to have discovered that the high interference actually observed was inconsistent with Doppler's principle and the theory of gases, I gave a more complete calculation *, taking into account the variable velocity of the molecules as defined by Maxwell's law, from which it appeared that there was really no disagreement with observation. Michelson compared these theoretical results with those of his important observations upon light from vacuum-tubes and found an agreement which was thought sufficient, although there remained some points of uncertainty.

The same ground was traversed by Schönrock †, who made the notable remark that while the agreement was good for the monatomic gases it failed for diatomic hydrogen, oxygen, and nitrogen ; and he put forward the suggestion that in these cases the chemical atom, rather than the usual molecule, was to be regarded as the carrier of the emission-centres. By this substitution, entailing an increase of velocity in the ratio $\sqrt{2}:1$, the agreement was much improved.

While I do not doubt that Schönrock's comparison is substantially correct, I think that his presentation of the theory is confused and unnecessarily complicated by the introduction (in two senses) of the " width of the spectrum line," a quantity not usually susceptible of direct observation. Unless I misunderstand, what he calls the observed width is a quantity not itself observed at all but deduced from the visibility of interference bands by arguments which already assume Doppler's principle and the theory of gases. I do not see what is gained by introducing this quantity. Given the nature of the radiating gas and its temperature, we can calculate from known data the distribution of light in the bands corresponding to any given retardation, and from photometric experience we can form a pretty good judgment as to the maximum retardation at which they should still be visible. This theoretical result can then be compared with a purely experimental one, and an agreement will confirm the principles on which the calculation was founded. I think it desirable to include here a sketch of this treatment of the question on the lines followed in 1889, but with a few slight changes of notation.

The phenomenon of interference in its simplest form occurs when two equal trains of waves are superposed, both trains having the same frequency and one being retarded relatively

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* " On the limits to interference when light is radiated from moving molecules," Phil. Mag. vol. xxvii. p. 298 (1889) ; Scientific Papers, vol. iii. p. 258.

† *Ann. der Physik*, xx. p. 995 (1906).

to the other by a linear retardation X *.   Then if λ denote the wave-length, the aggregate may be represented

$$\cos nt + \cos (nt - 2\pi X/\lambda) = 2 \cos (\pi X/\lambda) . \cos (nt - \pi X/\lambda). \quad (1)$$

The intensity is given by

$$I = 4 \cos^2 (\pi X/\lambda) = 2\{1 + \cos (2\pi X/\lambda)\}. \quad . \quad . \quad (2)$$

If we regard X as gradually increasing from zero, I is periodic, the maxima (4) occurring when X is a multiple of λ and the minima (0) when X is an odd multiple of $\frac{1}{2}\lambda$.   If bands are visible corresponding to various values of X, the darkest places are absolutely devoid of light, and this remains true however great X may be, that is however high the order of interference.

The above conclusion requires that the light (duplicated by reflexion or otherwise) should have an absolutely definite frequency, *i.e.*, should be absolutely homogeneous. Such light is not at our disposal; and a defect of homogeneity will usually entail a limit to interference, as X increases. We are now to consider the particular defect arising in accordance with Doppler's principle from the motion of the radiating particles in the line of sight.   Maxwell showed that for gases in temperature equilibrium the number of molecules whose velocities resolved in three rectangular directions lie within the range $d\xi\, d\eta\, d\zeta$ must be proportional to

$$e^{-\beta(\xi^2 + \eta^2 + \zeta^2)} d\xi\, d\eta\, d\zeta.$$

If ξ be the direction of the line of sight, the component velocities η, ζ are without influence in the present problem. All that we require to know is that the number of molecules for which the component ξ lies between ξ and $\xi + d\xi$ is proportional to

$$e^{-\beta\xi^2} d\xi. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The relation of β to the mean (resultant) velocity v is

$$v = \frac{2}{\sqrt{(\pi\beta)}} . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

It was in terms of v that my (1889) results were expressed, but it was pointed out that v needs to be distinguished from the velocity of mean square with which the pressure is more directly connected.   If this be called v',

$$v' = \sqrt{\left(\frac{3}{2\beta}\right)}. \quad . \quad . \quad . \quad . \quad (5)$$

so that

$$\frac{v}{v'} = \sqrt{\left(\frac{8}{3\pi}\right)} . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

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* In the paper of 1889 the retardation was denoted by 2Δ.

Again, the relation between the original wave-length Λ and the actual wave-length λ, as disturbed by the motion, is

$$\frac{\Lambda}{\lambda} = 1 + \frac{\xi}{c}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (7)$$

c denoting the velocity of light. The intensity of the light in the interference bands, so far as dependent upon the molecules moving with velocity ξ, is by (2)

$$d\mathrm{I} = 2\left\{1 + \cos\frac{2\pi\mathrm{X}}{\Lambda}\left(1 + \frac{\xi}{c}\right)\right\} e^{-\beta\xi^2} d\xi, \quad \cdot \quad \cdot \quad (8)$$

and this is now to be integrated with respect to ξ between the limits $\pm\infty$. The bracket in (8) is

$$1 + \cos\frac{2\pi\mathrm{X}}{\Lambda}\cos\frac{2\pi\mathrm{X}\xi}{\Lambda c} - \sin\frac{2\pi\mathrm{X}}{\Lambda}\sin\frac{2\pi\mathrm{X}\xi}{\Lambda c}.$$

The third term, being uneven in ξ, contributes nothing. The remaining integrals are included in the well-known formula

$$\int_{-\infty}^{+\infty} e^{-a^2x^2}\cos\left(2rx\right) dx = \frac{\sqrt{\pi}}{a} e^{-r^2/a^2}.$$

Thus

$$\mathrm{I} = \frac{2\sqrt{\pi}}{\sqrt{\beta}}\left[1 + \cos\frac{2\pi\mathrm{X}}{\Lambda} \cdot \mathrm{Exp}\left(-\frac{\pi^2\mathrm{X}^2}{c^2\beta\Lambda^2}\right)\right]. \quad \cdot \quad (9)$$

The intensity I_1 at the darkest part of the bands is found by making X an odd multiple of $\frac{1}{2}\lambda$, and I_2 the maximum brightness by making X a multiple of λ.
Thus

$$\mathrm{Exp}\left(-\frac{\pi^2\mathrm{X}^2}{c^2\beta\Lambda^2}\right) = \frac{\mathrm{I}_2 - \mathrm{I}_1}{\mathrm{I}_2 + \mathrm{I}_1} = \mathrm{V}, \quad \cdot \quad \cdot \quad (10)$$

where V denotes the "visibility" according to Michelson's definition. Equation (10) is the result arrived at in my former paper, and β can be expressed in terms of either the mean velocity v, or preferably of the velocity of mean square v' *.

The next question is what is the smallest value of V for which the bands are recognizable. Relying on photometric experience, I estimated that a relative difference of 5 per cent. between I_1 and I_2 would be about the limit in the case of high interference bands, and I took $\mathrm{V} = \cdot025$. Shortly afterwards † I made special experiments upon bands well

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* See also Proc. Roy. Soc. vol. lxxvi. A. p. 440 (1905); Scientific Papers, vol. v. p. 261.
† Phil. Mag. vol. xxvii. p. 484 (1889); Scientific Papers, vol. iii. p. 277.

under control, obtained by means of double refraction, and I found that in this very favourable case the bands were still just distinctly seen when the relative difference between I_1 and I_2 was reduced to 4 per cent. It would seem then that the estimate $V = \cdot025$ can hardly be improved upon. On this basis (10) gives in terms of v

$$\frac{X}{\Lambda} = \frac{2c}{\pi^{3/2}v} \sqrt{(\log_e 40)} = \cdot690\frac{c}{v}, \quad \cdot \quad \cdot \quad \cdot \quad (11)$$

as before. In terms of v' by (6)

$$\frac{X}{\Lambda} = \frac{\sqrt{3}\cdot c}{\pi\sqrt{2}\cdot v'} \sqrt{(\log_e 40)} = \cdot749\frac{c}{v'}. \quad \cdot \quad \cdot \quad (12)$$

As an example of (12), let us apply it to hydrogen molecules at $0°$ C. Here $v' = 1839 \times 10^2$ cm./sec.[*], and $c = 3 \times 10^{10}$. Thus

$$X/\Lambda = 1\cdot222 \times 10^5. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (13)$$

This is for the hydrogen *molecule*. For the hydrogen *atom* (13) must be divided by $\sqrt{2}$. Thus for absolute temperature T and for radiating centres whose mass is m times that of the hydrogen *atom*, we have

$$\frac{X}{\Lambda} = \frac{1\cdot222 \times \sqrt{(273)} \times 10^5}{\sqrt{2}} \sqrt{\left(\frac{m}{T}\right)} = 1\cdot427 \times 10^6 \sqrt{\left(\frac{m}{T}\right)}.$$
$$\cdot \quad \cdot \quad \cdot \quad (14)$$

In Buisson and Fabry's corresponding formula, which appears to be derived from Schönrock, $1\cdot427$ is replaced by the appreciably different number $1\cdot22$.

The above value of X is the retardation corresponding to the *limit* of visibility, taken to be represented by $V = \cdot025$. In Schönrock's calculation the retardation X_1, corresponding to $V = \cdot5$, is considered. In (12), $\sqrt{(\log_e 40)}$ would then be replaced by $\sqrt{(\log_e 2)}$, and instead of (14) we should have

$$\frac{X_1}{\Lambda} = 6\cdot186 \times 10^5 \sqrt{\left(\frac{m}{T}\right)}. \quad \cdot \quad \cdot \quad \cdot \quad (15)$$

But I do not understand how $V = \cdot5$ could be recognized in practice with any precision.

Although it is not needed in connexion with high interference, we can of course calculate the width of a

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[*] It seems to be often forgotten that the first published calculation of molecular velocities was that of Joule (Manchester Memoirs, Oct. 1848; Phil. Mag. ser. 4, vol. xiv. p. 211.)

spectrum line according to any conventional definition. Mathematically speaking, the width is infinite; but if we disregard the outer parts where the intensity is less than *one-half* the maximum, the limiting value of ξ by (3) is given by

$$\beta\xi^2 = \log_e 2, \quad \cdots \quad \cdots \quad (16)$$

and the corresponding value of λ by

$$\frac{\lambda-\Lambda}{\Lambda} = \frac{\xi}{c} = \frac{\sqrt{(\log_e 2)}}{c\sqrt{\beta}}. \quad \cdots \quad (17)$$

Thus, if $\delta\lambda$ denote the half-width of the line according to the above definition,

$$\frac{\delta\lambda}{\Lambda} = \frac{\sqrt{(\cdot6931)}}{c\sqrt{\beta}} = 3\cdot57 \times 10^{-7}\sqrt{\left(\frac{T}{m}\right)}, \quad \cdots \quad (18)$$

T denoting absolute temperature and m the mass of the particles in terms of that of the hydrogen atom, in agreement with Schönrock.

In the application to particular cases the question at once arises as to what we are to understand by T and m. In dealing with a flame it is natural to take the temperature of the flame as ordinarily understood, but when we pass to the rare vapour of a vacuum-tube electrically excited the matter is not so simple. Michelson assumed from the beginning that the temperature with which we are concerned is that of the tube itself or not much higher. This view is amply confirmed by the beautiful experiments of Buisson and Fabry [*], who observed the limit of interference when tubes containing helium, neon, and krypton were cooled in liquid air. Under these conditions bands which had already disappeared at room temperature again became distinct, and the ratios of maximum retardations in the two cases (1·66, 1·60, 1·58) were not much less than the theoretical 1·73 calculated on the supposition that the temperature of the gas is that of the tube. The highest value of X/Λ, in their notation N, hitherto observed is 950,000, obtained from krypton in liquid air. With all three gases the agreement at room temperature between the observed and calculated values of N is extremely good, but as already remarked their theoretical numbers are a little lower than mine (14). We may say not only that the observed effects are accounted for almost completely by Doppler's principle and the theory of gases, but that

[*] *Journ. de Physique*, t. ii. p. 442 (1912).

the temperature of the emitting gas is not much higher than that of the containing tube.

As regards m, no question arises for the inert monatomic gases. In the case of hydrogen Buisson and Fabry follow Schönrock in taking the atom rather than the molecule as the moving source, so that $m=1$; and further they find that this value suits not only the lines of the first spectrum of hydrogen but equally those of the second spectrum whose origin has sometimes been attributed to impurities or aggregations.

In the case of sodium, employed in a vacuum-tube, Schönrock found a fair agreement with the observations of Michelson, on the assumption that the *atom* is in question. It may be worth while to make an estimate for the D lines from soda in a Bunsen flame. Here $m=23$, and we may perhaps take T at 2500. These data give in (14) as the maximum number of bands

$$X/\Lambda = 137,000.$$

The number of bands actually seen is very dependent upon the amount of soda present. By reducing this Fizeau was able to count 50,000 bands, and it would seem that this number cannot be much increased[*], so that observation falls very distinctly behind calculation[†]. With a large supply of soda the number of bands may drop to two or three thousand, or even further.

The second of the possible causes of loss of homogeneity enumerated above, viz. *rotation* of the emitting centres, was briefly discussed many years ago in a letter to Michelson[‡], where it appeared that according to the views then widely held this cause should be more potent than (i.). The transverse vibrations emitted from a luminous source cannot be uniform in all directions, and the effect perceived in a fixed

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[*] "Interference Bands and their Applications," Nature, vol. xlviii. p. 212 (1893); Scientific Papers, vol. iv. p. 59. The parallel plate was a layer of water superposed upon mercury. An enhanced illumination may be obtained by substituting nitro-benzol for water, and the reflexions from the mercury and oil may be balanced by staining the latter with aniline blue. But a thin layer of nitro-benzol takes a surprisingly long time to become level.

[†] Smithells (Phil. Mag. xxxvii. p. 245, 1894) argues with much force that the actually operative parts of the flame may be at a much higher temperature (if the word may be admitted) than is usually supposed, but it would need an almost impossible allowance to meet the discrepancy. The chemical questions involved are very obscure. The coloration with soda appears to require the presence of oxygen (Mitcherlich, Smithells).

[‡] Phil. Mag. vol. xxxiv. p. 407 (1892); Scientific Papers, vol. iv. p. 15.

direction from a rotating source cannot in general be simple harmonic. In illustration it may suffice to mention the case of a bell vibrating in four segments and rotating about the axis of symmetry. The sound received by a stationary observer is intermittent and therefore not homogeneous. On the principle of equipartition of energy between translatory and rotatory motions, and from the circumstance that the dimensions of molecules are much less than optical wavelengths, it followed that the loss of homogeneity from (ii.) was much greater than from (i.). I had in view diatomic molecules—for at that time mercury vapour was the only known exception ; and the specific heats at ordinary temperatures showed that two of the possible three rotations actually occurred in accordance with equipartition of energy. It is now abundantly clear that the widening of spectrum lines at present under consideration does not in fact occur ; and the difficulty that might be felt is largely met when we accept Schönrock's supposition that the radiating centres are in all cases monatomic. Still there are questions remaining behind. Do the atoms rotate, and if not why not? I suppose that the quantum theory would help here, but it may be noticed that the question is not merely of acquiring rotation. A permanent rotation, not susceptible of alteration, should apparently make itself felt. These are problems relating to the constitution of the atom and the nature of radiation, which I do not venture further to touch upon.

The third cause of widening is the disturbance of free vibration due to encounters with other bodies. That something of this kind is to be expected has long been recognized, and it would seem that the widening of the D lines when more than a very little soda is present in a Bunsen flame can hardly be accounted for otherwise. The simplest supposition open to us is that an entirely fresh start is made at each collision, so that we have to deal with a series of regular vibrations limited at both ends. The problem thus arising has been treated by Godfrey [*] and by Schönrock [†]. The Fourier analysis of the limited train of waves of length r gives for the intensity of various parts of the spectrum line

$$k^{-2} \sin^2 (\pi r k), \quad \ldots \quad \ldots \quad (19)$$

where k is the reciprocal of the wave-length, measured from the centre of the line. In the application to radiating vapours, integrations are required with respect to r.

[*] Phil. Trans. A. vol. cxcv. p. 346 (1899). See also Proc. Roy. Soc. vol. lxxvi, A. p. 440 (1905) ; Scientific Papers, vol. v. p. 257.

[†] *Ann. der Physik*, vol. xxii. p. 209 (1907).

Calculations of this kind serve as illustrations; but it is not to be supposed that they can represent the facts at all completely. There must surely be encounters of a milder kind where the free vibrations are influenced but yet not in such a degree that the vibrations after the encounter have no relation to the previous ones. And in the case of flames there is another question to be faced: Is there no distinction in kind between encounters first of two sodium atoms and secondly of one sodium atom and an atom say of nitrogen? The behaviour of soda flames shows that there is. Otherwise it seems impossible to explain the great effect of relatively very small additions of soda in presence of large quantities of other gases. The phenomena suggest that the failure of the least coloured flames to give so high an interference as is calculated from Doppler's principle may be due to encounters with other gases, but that the rapid falling off when the supply of soda is increased is due to something special. This might be of a quasi-chemical character, *e. g.* temporary associations of atoms; or again to vibrators in close proximity putting one another out of tune. In illustration of such effects a calculation has been given in the previous paper [*]. It is in accordance with this view that, as Gouy found, the emission of light tends to increase as the square root of the amount of soda present.

We come now to cause (iv.). Although it is certain that this cause must operate, we are not able at the present time to point to any experimental verification of its influence. As a theoretical illustration " we may consider the analysis by Fourier's theorem of a vibration in which the amplitude follows an exponential law, rising from zero to a maximum and afterwards falling again to zero. It is easily proved that

$$e^{-a^2 x^2} \cos rx = \frac{1}{2a \sqrt{\pi}} \int_0^\infty du \cos ux \{ e^{-(u-r)^2/4a^2} + e^{-(u+r)^2/4a^2} \},$$

$$. \quad . \quad . \quad (20)$$

in which the second member expresses an aggregate of trains of waves, each individual train being absolutely homogeneous. If a be small in comparison with r, as will happen when the amplitude on the left varies but slowly, $e^{-(u+r)^2/4a^2}$ may be neglected, and $e^{-(u-r)^2/4a^2}$ is sensible only when u is very nearly equal to r " [†].

An analogous problem, in which the vibration is repre-

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[*] Phil. Mag. *suprà*, p. 209.

[†] Phil. Mag. vol. xxxiv. p. 407 (1892); Scientific Papers, vol. iv. p. 16.

sented by $e^{-at}\sin bt$, has been treated by Garbasso [*]. I presume that the form quoted relates to positive values of t and that for negative values of t it is to be replaced by zero. But I am not able to confirm Garbasso's formula [†].

As regards the fifth cause of (additional) widening enumerated at the beginning of this paper, the case is somewhat similar to that of the fourth. It must certainly operate, and yet it does not appear to be important in practice. In such rather rough observations as I have made, it seems to make no great difference whether two surfaces of a Bunsen soda flame (front and back) are in action or only one. If the supply of soda to each be insufficient to cause dilatation, the multiplication of flames in line (3 or 4) has no important effect either upon the brightness or the width of the lines. Actual measures, in which no high accuracy is needed, would here be of service.

The observations referred to led me many years ago to make a very rough comparison between the light actually obtained from a nearly undilated soda line and that of the corresponding part of the spectrum from a black body at the same temperature as the flame. I quote it here rather as a suggestion to be developed than as having much value in itself. Doubtless, better data are now available.

How does the intrinsic brightness of a just undilated soda flame compare with the total brightness of a black body at the temperature of the flame? As a source of light Violle's standard, viz., one sq. cm. of just melting platinum, is equal to about 20 candles. The candle presents about 2 sq. cm. of area, so that the radiating platinum is about 40 as bright. Now platinum is not a black body and the Bunsen flame is a good deal hotter than the melting metal. I estimated (and perhaps under estimated) that a factor of 5 might therefore be introduced, making the black body at flame temperature 200 as bright as the candle.

To compare with a candle a soda flame of which the D-lines were just beginning to dilate, I reflected the former nearly perpendicularly from a single glass surface. The soda flame seemed about half as bright. At this rate the intrinsic brightness of the flame was $\frac{1}{2} \times \frac{1}{25} = \frac{1}{50}$ of that of the candle, and accordingly $\frac{1}{10,000}$ of that of the black body.

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[*] *Ann. der Physik*, vol. xx. p. 848 (1906).
[†] Possibly the sign of a is supposed to change when t passes through zero. But even then what are perhaps misprints would need correction.

The black body gives a continuous spectrum. What would its brightness be when cut down to the narrow regions occupied by the D-lines? According to Abney's measures the brightness of that part of sunlight which lies between the D's would be about $\frac{1}{250}$ of the whole. We may perhaps estimate the region actually covered by the soda lines as $\frac{1}{25}$ of this. At this rate we should get

$$\frac{1}{25} \times \frac{1}{250} = \frac{1}{6250},$$

as the fraction of the whole radiation of the black body which has the wave-lengths of the soda lines. The actual brightness of a soda flame is thus of the same order of magnitude as that calculated for a black body when its spectrum is cut down to that of the flame, and we may infer that the light of a powerful soda flame is due much more to the widening of the spectrum lines than to an increased brightness of their central parts.

Terling Place, Witham,
  Dec. 18.

XXXII. *The Spectra of Helium and Hydrogen.*
By E. J. Evans, *B.Sc., A.R.C.Sc.**

Introduction.

THE investigation of the series spectra of hydrogen and helium has acquired considerable importance in consequence of recent theories on the structure of the atom, and the application of the quantum hypothesis to radiation problems.

It is known that some of the series spectra attributed to hydrogen can be represented with great accuracy by the Balmer-Rydberg-Ritz formula

$$\nu = \mathrm{K}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right), \quad \ldots \quad \ldots \quad (1)$$

where ν represents the frequency, K Rydberg's universal constant, and n_1 and n_2 are whole numbers. If in equation (1) $n_1 = 2$, and n_2 takes the successive values 3, 4, 5 . . . . . , the ordinary hydrogen series in the visible spectrum is

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* Communicated by Sir E. Rutherford, F.R.S.

obtained. The formula for this series was discovered by Balmer, and the series is usually referred to as the Balmer series. If $n_1 = 3$ a series of lines in the ultra-red is obtained, and two members of this series have been observed by Paschen. Also the series calculated by putting $n_1 = 1$ has been recently observed by Lyman [*] in the extreme ultra-violet. In addition to the lines represented by formula (1), some other series of lines have generally been ascribed to hydrogen. In 1896 Pickering [†] discovered in the spectrum of the star ξ Puppis a series of lines, which are closely represented by the formula

$$\nu = K \left\{ \frac{1}{2^2} - \frac{1}{(n + \frac{1}{2})^2} \right\} \quad . \quad . \quad . \quad . \quad (2)$$

On account of the numerical relationships existing between this series and the Balmer series, Pickering attributed the lines to hydrogen, and later Rydberg [‡], from analogy with the spectra of the alkali metals, considered the Balmer and Pickering series to be the diffuse and sharp series of hydrogen. He further concluded that the complete hydrogen spectrum should contain another series of lines, corresponding to the principal series in the spectra of the alkali metals, and given by the formula

$$\nu = K \left\{ \frac{1}{(1\frac{1}{2})^2} - \frac{1}{(n + 1)^2} \right\} . \quad . \quad . \quad . \quad (3)$$

Rydberg's conclusions were apparently strongly supported by the observation of a strong line in the spectra of certain stars and nebulæ at the place calculated for the first line in formula (3).

A few years ago, Fowler [§] obtained the two series of lines represented by equations (2) and (3) by passing a condensed discharge from a 10-inch coil through mixtures of helium and hydrogen contained in an ordinary Plücker tube. Further, he observed in the spectrum of the mixed gases a third series related to the series represented by equation (3) in the same way as the Pickering series is related to the Balmer series, and which was approximately represented by the formula

$$\nu = K \left\{ \frac{1}{(1\frac{1}{2})^2} - \frac{1}{(n + \frac{1}{2})^2} \right\} . \quad . \quad . \quad . \quad (4)$$

[*] Lyman, 'Nature,' xciii. p. 241.
[†] Pickering, Astro-Phys. Journ. vol. iv. p. 369 (1896) ; vol. v. p. 92 (1897).
[‡] Rydberg, Astro-Phys. Journ. vol. vii. p. 233 (1899).
[§] Fowler, Monthly Notices R. A. S., Dec. 1912.

Fowler, in the absence of strict experimental proof, considered that Rydberg's theoretical investigations justified the conclusion that the three series of lines were due to hydrogen, and the series represented by (4) was called the second principal series of hydrogen. It is interesting to note that with the observation of series (4) the supposed analogy between the spectra of hydrogen and the alkali metals breaks down, as the spectra of the latter are known to have only one principal series.

Recently the problem of the origin of the series in question has been considered from the theoretical standpoint by Dr. Bohr*, who has arrived at very interesting results. Taking as basis Sir E. Rutherford's † atom-model, he has deduced with the aid of Planck's quantum hypothesis the following formula for the spectrum emitted by an atomic system consisting of a central positive nucleus and an electron moving round it :

$$\nu = \frac{2\pi^2 e^2 E^2 M m}{h^3 (M+m)} \left\{ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right\}, \quad \cdot \quad \cdot \quad \cdot \quad (5)$$

where e and m are the charge and mass of the electron, $\dot{E}$ and M the charge and mass of the nucleus, and h is Planck's constant. For a hydrogen atom according to Rutherford's theory, $E = -e$, and the formula can be written

$$\nu = \frac{2\pi^2 e^4 m}{h^3 \left(1 + \dfrac{m}{M} \right)} \left\{ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right\} \quad \cdot \quad \cdot \quad \cdot \quad (6)$$

where the bracket multiplying h^3 is very nearly equal to unity on account of the great mass of the nucleus compared with that of the electron. It was shown by Bohr that the above expression, on putting in the values of the constants, agreed within the limits of experimental error with formula (1).

It will be seen that formula (6) does not include the lines observed by Pickering and Fowler, and given by formulæ (2), (3), and (4). However, if in equation (5) $E = -2e$, which according to Rutherford represents the helium atom, the following formula is obtained for the frequency of the lines :

$$\nu = \frac{2\pi^2 e^4 m}{h^3 \left(1 + \dfrac{m}{M} \right)} \left\{ \frac{1}{\left(\dfrac{n_1}{2} \right)^2} - \frac{1}{\left(\dfrac{n_2}{2} \right)^2} \right\} \quad \cdot \quad \cdot \quad \cdot \quad (7)$$

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* N. Bohr, Phil. Mag. xxvi. pp. 1, 476, 857 (1913) ; xxvii. p. 506 (1914).

† Sir E. Rutherford, Phil. Mag. xxi. p. 669 (1911).

As the factor outside the bracket differs from that in formula (6) only by a small correction due to the difference in the masses of the hydrogen and helium nuclei, it will be seen that equation (7) approximately represents the series of lines given by (2), (3), and (4). Bohr therefore suggested that the lines in question were not due to hydrogen but to helium. This conclusion was not disproved by previous observations and experiments, for helium was always known to be present when the lines appeared. Bohr also pointed out that the reason why the lines considered are not observed in ordinary helium tubes may be that in such tubes the ionization of the gas is not as complete as in the star ξ Puppis or in Fowler' experiments with the condensed discharge. According to the theory, the presence of helium atoms which have lost both electrons is necessary for the appearance of these lines in a spectrum-tube.

Preliminary experiments by the author * gave strong support to Bohr's conclusions. A helium spectrum was obtained showing the first line (λ 4686) of the series represented by equation (3) very brightly, but no trace of the ordinary hydrogen lines of the Balmer series. Also this line could not be observed in the spectrum obtained by passing a strong discharge through mixtures of hydrogen and neon, and of hydrogen and argon. Later Stark † observed the 4686 line in a helium tube in which the hydrogen lines did not appear. Further evidence pointing to the same conclusion has been given by Rau ‡, who has made some interesting experiments on the voltage necessary for the production of spectrum lines.

In a discussion in 'Nature,' Fowler § pointed out that the lines observed by him were not accurately represented by formulæ (2), (3), and (4), but Bohr ‖ subsequently showed that the deviations from the values given by the formulæ could be accounted for within the limits of experimental error by taking into account the correction due to the mass of the central nucleus. This influence of the mass of the nucleus was not considered in Bohr's original paper. Recently Fowler¶ has published a very important paper on series lines in spark spectra. He concludes from analogy with spark spectra of the enhanced type, that the lines represented by equations (2), (3), and (4) are enhanced lines

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* Evans, 'Nature,' xcii. p. 5.
† Stark, *Verh. d. Deutsch. Phys. Ges.* xvi. p. 468 (1914).
‡ Rau, *Sitzungsb. d. Phys.-Med. Ges. Würzburg*, 1914.
§ Fowler, 'Nature,' xcii. p. 95.   ‖ Bohr, 'Nature,' xcii. p. 231.
¶ Fowler, Phil. Trans. A. vol. ccxiv. p. 225.

of helium. Stark also came to the same conclusion with respect to the line 4686.

In the above mentioned discussion in 'Nature' Bohr showed that if his view was correct, the helium spectrum should contain another series of lines, which are represented by the formula

$$\nu = K' \left\{ \frac{1}{(2)^2} - \frac{1}{(n)^2} \right\} \quad . \quad . \quad . \quad . \quad (8)$$

where K' is the constant outside the bracket in formula (7). This formula is obtained from (7) by putting $n_1 = 4$ and $n_2 = 6, 8, 10 \ldots$. The lines of this series should appear near the hydrogen lines of the Balmer series, and their wave-lengths were calculated to be 6560·4, 4859·5, 4338·9, 4100·2 . . . . . These lines and the Pickering lines can be represented by one formula

$$\nu = K' \left\{ \frac{1}{(2)^2} - \frac{1}{\left(\frac{n}{2}\right)^2} \right\} \quad . \quad . \quad . \quad . \quad (9)$$

and the intensity of all the lines should decrease regularly with increasing values of n. The lines would be difficult to detect, especially if hydrogen was present in any quantity, as it is known from Fowler's experiments that the Pickering lines are faint even when photographed with instruments of small dispersion. The presence of the lines given by formula (8) would greatly strengthen the experimental evidence in favour of Bohr's theory, but their absence would immediately show that the theory was incorrect. The investigation of the lines in question, and the determination of more accurate values for the wave-lengths of the lines of the Pickering series, formed the main object of the present research.

The Experimental Arrangement.

The method which was chiefly employed for the production of the spectrum lines was very similar to that previously described by Fowler. A 20-inch coil with a condenser across its terminals was connected to a helium spectrum-tube in series with which was placed an adjustable spark-gap. The spectrum produced was examined visually with a Hilger direct-reading instrument, and the wave-lengths could be read off with an accuracy of 1 or 2 A.U. For the purpose of photographing the lines, four different instruments were employed. In the first series of experiments the lines were photographed by means of a small quartz spectrograph giving

a dispersion of 250 A.U. per mm. in the red, 130 A.U. per mm. in the green, and 76 A.U. per mm. in the violet. Later the spectrum was photographed with a concave grating of 1 metre radius ruled with 14,000 lines to the inch. By means of this instrument it was found possible to obtain the first members of series (3) and (4), but no trace of any of the lines represented by equations (2) and (8) even after exposures of 40 hours. A few members of the series represented by equation (2) were obtained in the first place by employing a spectroscope consisting of two glass prisms, which gave a dispersion of 150 A.U. per mm. in the red, 54 A.U. per mm. in the green, and 30 A.U. per mm. in the violet. Finally these two prisms were replaced by others giving greater dispersion and capable of resolving 2 A.U. at λ 6500. For the sake of comparison the dispersions given by this prism spectroscope in the red, green, and violet were 75, 27, and 15 A.U. per mm. respectively. The time of exposure varied from 20 minutes to 30 hours, depending upon the dispersion of the apparatus and the particular lines studied. The first member of series (3) at 4686 was easily photographed, but the series represented by formula (9) required a very long exposure, and even then only a few members of the series could be detected with certainty. All the photographs were taken with Wratten and Wainwright's panchromatic plates and films.

The spectrum-tubes employed were of various shapes and dimensions. The diameter of the capillary was varied from ·8 to 3·5 mm., and its length from 3 to 8 cm. When the lines represented by equation (9) were studied, a spectrum-tube with a capillary of ·8 mm. was chosen, the spark-gap was made 1·2 cm., and the pressure of the helium was adjusted to about ·5 mm. of mercury. Photographs of the 4686 line were taken with spectrum-tubes having capillaries of different bore, and containing helium at pressures ranging from ·36 to 2 mm.

Since the hydrogen lines of the Balmer series are in ordinary circumstances much stronger than the odd members of series (9), it was necessary, especially with the relatively small dispersion employed, to obtain a helium spectrum giving little or no trace of the hydrogen lines. In the preliminary experiments spectrum-tubes with aluminium electrodes were employed, but it was found impossible to remove the hydrogen from the electrodes in a reasonable time. Later, thin platinum electrodes of ·4 mm. diameter were employed, and a helium spectrum showing no trace of hydrogen was obtained. In this connexion it is interesting

to note that it is comparatively easy to obtain a helium
spectrum showing no trace of the hydrogen lines of the
Balmer series if an ordinary discharge is sent through a
spectrum tube containing purified helium.   With the con-
denser discharge, however, the hydrogen lines usually appear
in the bulbs, although they are often not present in the
capillary.   This was also observed by Curtis * during a
research on the band spectrum of helium.

The arrangement of the apparatus and the method of con-
ducting the experiments are made clear by reference to the
accompanying diagram.
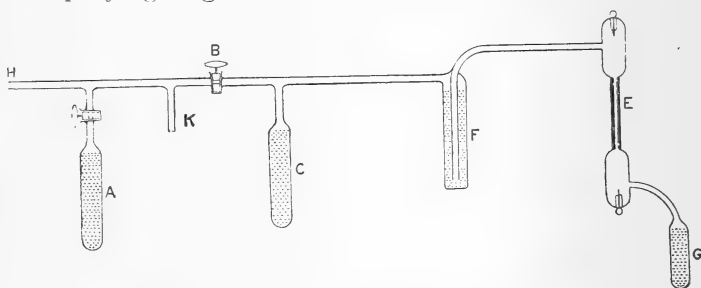
In the diagram, E represents the spectrum tube and A,
C, F, and G bulbs containing carefully prepared coconut
charcoal.   The tap B was placed at a distance of 1 metre
from the spectrum-tube, and the discharge scarcely ever
reached it.   A Töpler pump and a tube of P_2O_5 were attached
to H, and the whole apparatus was evacuated to a pressure
of 1/100th of a mm. of mercury.   The charcoal bulbs C, F,
and G were then heated for several hours until no more gas
was given off.   Also the bulbs and the capillary of the
spectrum-tube were heated until the softening point of glass
was reached.   The gases given off during the heating process
were absorbed by the charcoal bulb A, which was immersed
in liquid air.   The tap B was then closed and the gas
absorbed by the charcoal in A removed by heating.
The bulb A was again immersed in liquid air, and the helium
containing a small quantity of impurities was then introduced
through the side-tube K and allowed to remain in that part
of the apparatus for over an hour.   The charcoal bulbs C, F,
and G were now immersed in liquid air, and the tap B was
opened so that helium could enter the spectrum-tube.   The
pressure of the gas was then adjusted to ·3 mm. by means of
the pump and McLeod gauge, and the ordinary discharge
(without condenser) passed through the tube.   The current

* Curtis, Proc. Roy. Soc. A. vol. lxxxix. p. 146 (1913).

passing through the primary of the induction-coil was adjusted until the cathode was almost white-hot, and it was kept at this temperature for nearly four hours. By reversing the direction of the current passing through the tube, the other electrode was treated in a similar manner. This process was repeated until no hydrogen lines were visible in the Hilger direct-reading spectroscope. The condenser discharge was then passed through the tube for 30 minutes, and both the bulbs and capillary were examined for the presence of the hydrogen lines. If the lines eventually appeared, the process of heating the electrodes was continued until the spectrum showed no hydrogen lines after the passage of a heavy condenser discharge for one hour. During these experiments the platinum electrodes spluttered to the sides of the spectrum-tube and consequently became much finer. This was also made evident by the bending of the electrodes to touch the sides of the bulbs when a heavy condenser discharge was passed through the tube. In later experiments, the diameters of the bulbs were so adjusted that the platinum electrodes would not touch the sides even when perpendicular to their original directions. In the preliminary experiments, all the photographs and observations were obtained with the spectrum-tube in the vertical position, but later, especially when investigating the series represented by equation (9), the tube was usually placed in the end-on position with the capillary pointing towards the spectroscope.

The spectrum obtained by passing the ordinary discharge without condenser and spark-gap through a tube containing helium at a pressure of ·25 mm. was also studied. Under these conditions a stream of charged particles, which were deflected by a magnet in the same direction as cathode rays, passed down the tube. The results of experiments carried out in this way will be described later.

For the determination of wave-lengths, the lines of the ordinary helium spectrum were employed as standards except in the red and yellow, where they are too far apart. In these regions, the impurity lines of mercury, sodium, silicon, and oxygen were found useful. Also in some cases the wave-lengths were determined with the aid of a copper or barium comparison spectrum. The mercury lines only appeared on one of the plates, but the sodium, silicon, and oxygen lines were always present on photographs taken when a heavy condenser discharge was passed through the tube. These lines are due to the decomposition of the glass of the capillary by the discharge.

EXPERIMENTAL RESULTS.

The Series given by Formulæ (3) *and* (4).

The preliminary experiments * showed that it was possible to obtain photographs showing the 4686 line very strongly, and no trace of the ordinary hydrogen lines of the Balmer series. As the photographs were taken with a quartz spectrograph of small dispersion, the wave-length could only be determined with an accuracy of about 1 A.U. The line was therefore photographed with the prism spectroscope giving the greatest dispersion, and the wave-length determined with a greater degree of accuracy. The mean wave-length as determined from these photographs was 4686·00 (±·05), which agreed well with the value 4685·98 (±·01) determined by Fowler from a photograph taken with a 10-foot concave grating.

It was also possible to obtain this line, employing the same spectroscope, by passing the ordinary discharge without condenser and spark-gap through an end-on tube containing helium at a pressure of ·25 mm. The line is shown in photograph I. (Pl. VI.), where it appears fairly strong and broad in the capillary. The wave-length of the line was measured and found to be 4685·94. The photograph does not show the presence of the hydrogen lines at 6563, 4861, ... but only the ordinary helium lines and the 4686 line.

These experiments show that it is possible to obtain the first member of series (3) from a helium tube giving no trace of the hydrogen lines of the Balmer series.

The Series given by Formula (9).

(A) *Experiments with tubes containing aluminium electrodes.*

The second member of this series was observed visually for the first time in the spectrum of an end-on tube with a narrow capillary. Two members of the series are shown in photograph II., which was taken with the two-prism spectroscope of low dispersion. The wave-lengths of these lines were determined with an accuracy of 0·2 A.U., and were found to agree within the limits of experimental error with the values calculated for the second and fourth members of series (9). The two values obtained were 5411·63 and 4541·93 respectively. The wave-lengths of the lines as determined by Fowler were 5410·5(±1·0) and 4541·3(±0·25). In addition to the ordinary helium lines, shorter or capillary

* Evans, *loc. cit.*

lines due to oxygen, silicon, and sulphur made their appearance in the spectrum. The photograph also shows the presence of the $H_a (6563)$, $H_\beta (4861)$ .... lines of hydrogen and the mercury line at 5460. These lines stretch across the capillary and have the same length as the ordinary helium lines. The 5411 and the 4542 lines also pass through the capillary spectrum, but their lengths are only about one half of that of the ordinary helium lines. The line at 5411 was also found to be more intense and sharper than the 4542 line. The sixth member of series (9) could not be detected on the photographic plate. A thorough examination of the plate near the H_a and H_β lines did not reveal the presence of any faint lines at 6560·4 and 4859·5. Rough measurements, however, showed that the widths of the H_a and H_β lines were approximately 8·1 and 5 A.U. respectively. Also the line at 5411 was found to be narrow compared with the hydrogen lines. Since the even members of series (9) were so faint compared with the hydrogen lines, it was decided to repeat the experiments with a prism spectroscope of nearly double the dispersion and tubes provided with thin platinum electrodes.

(B) *Experiments with spectrum tubes provided with platinum electrodes.*

A condenser discharge was sent through an end-on tube containing helium at a pressure of ·4 mm., and three photographs were taken with the two-prism spectroscope of greatest dispersion after exposures of 5, 12, and 26 hours respectively. In the last case the direction of the discharge was reversed at the end of 13 hours. On all the plates a faint line appeared at 6560, which is the calculated position for the first line of series (9). This line was shorter than the ordinary helium lines, and the oxygen lines at 6455 and 6157, but longer than the silicon capillary lines at 6371 and 6347.

The plates taken with exposures of 12 and 26 hours showed in addition to the 6560 line an ill-defined capillary line at 6564. The nature of the line made accurate measurements impossible, and the origin of the line is unknown unless it is due to a trace of hydrogen. On the same plate there also appeared a line at 5411, which was of the same general character as the 6560 line but of less intensity. The third member of the series at 4859·5 could not be detected on the plates taken with exposures of 5 and 12 hours, and the only lines present in this region were the oxygen capillary lines at 4872, 4865, 4861, and 4857. The plate taken with an

exposure of 26 hours was also examined in the same region, and the wave-lengths of two very faint lines, which extended beyond the capillary, were measured. One of these lines, which had a wave-length of 4861·7 A.U., was longer than the 6560 line. The other line was fainter than the 4861 line, and its measured wave-length was 4859·5. The fourth member of the series which should appear at 4542 could not be detected on any of the plates. All the lines between 7065 and 4713 on the plate taken with an exposure of 12 hours were measured, and with the exception of capillary lines at 6721·5, 6641·1, 5739·3, 4829·3, 4813·7, all the others could be attributed to helium, oxygen, silicon, sodium, and chlorine. These experiments show that when a condenser discharge was passed through helium, two lines were obtained whose wave-lengths agreed within the limits of experimental error with the values calculated for the first and second members of series (9), and whose intensities fell off with diminishing wave-length. Also a very faint line was obtained whose wave-length was very approximately the same as that calculated for the third member of the series represented by equation (9). However, in view of the faintness of the line and the appearance of another stronger line of unknown origin close to it, the question whether the line is the third member of the series cannot be regarded as settled.

The experiments described above show that very long exposures are required to bring out the lines of the series given by equation (9), for even with exposures of 26 hours only two lines could be detected with certainty. It was therefore considered desirable to obtain photographs with the other prism spectroscope, which gave a lower dispersion. Two photographs were taken, one with an exposure of 21 hours (photograph III.), and the other with an exposure of 31 hours. In the latter case, the discharge was reversed in direction at the end of half the exposure. The wave-lengths of the first two lines were measured for each plate, and found to be 6560·69, 5411·95, and 6560·10, 5411·71 respectively. A third line at 4860·5 was also obtained, but its wave-length was 1 A.U. greater than the value calculated theoretically for the third member of the series. Also, the line had too great an intensity if it was to be regarded as the third member of the series in which 6560 and 5411 were the first and second members respectively. It is interesting to point out that the wave-length (4860·5) is approximately the mean of the two values 4861·7 and 4859·5 obtained for the two faint lines photographed with the spectroscope of greater dispersion. The appearance of the line also suggested

that it might possibly be a double line. A faint fourth line of the right order of intensity in the blue region of the spectrum was also measured, and its wave-length (4542·2) is found to agree within the limits of experimental error with the calculated value (4541·80) for the fourth member of the series.

When the above exposures were concluded, the helium was pumped out of the spectrum-tube and replaced by oxygen. A condenser discharge was then sent through the tube for 4 hours, and a photograph taken. The lines on this plate between 6800 and 6157 were measured, and no evidence was found of the presence of a line at 6560. A line at 6563·5, probably due to hydrogen, was however obtained. The two lines at 6721 and 6641, and impurity lines due to nitrogen and silicon, were also present.

EXPERIMENTS WITH THE ORDINARY DISCHARGE.

In these experiments, the ordinary discharge was passed through an end-on tube containing helium at a pressure of ·25 mm. The same spectroscope was employed as in the experiments described in the last section, but the slit was widened in consequence of the comparatively small intensity of the light. The exposure was varied from 9 to 12 hours and a copper comparison spectrum was sometimes utilized for the determination of wave-lengths. The discharge was also reversed in direction when half the time of exposure had elapsed. A series of lines with wave-lengths approximately the same as those calculated from equation (9) appeared in the capillary in addition to the 4686 line. The wave-length measurements in this case were not as accurate as before, because of the greater breadth of the lines. The mean values of the wave-lengths obtained for the first four lines are 6560·71, 5411·44, 4860·5, 4542·44. For one of the photographs the measurements were extended still further towards the violet, and lines which are possible members of series (9) were obtained at 4339·97 and 4199·9. All the lines on this photograph (photograph IV.) between 6678 and 3819 were measured, and with the exception of the above lines and two others at 4358·7 and 4226·9, they were all due to helium and oxygen. In all the photographs taken with the ordinary discharge the third line at 4860·5 was stronger than it should be if it was the third member of series (9).

The accompanying table gives the wave-lengths of the lines which have been determined from photographs taken

with the condenser discharge and also the ordinary discharge, together with the values calculated from Bohr's theory. The values given for the first four lines were determined from photographic plates taken with the condenser discharge, whilst the last two values were deduced from photographs taken with the ordinary discharge. The dispersion in the particular region of the spectrum and the probable error are also included in the table.

Wave-length calculated.	Wave-length observed.	Limit of error.	Dispersion.
6560·38	6560·43	0·5	75 AU per mm.
5411·74	5411·67	0·2	45 AU per mm.
4859·54	?		
4541·80	4541·93	0·2	35 AU per mm.
4338·88	*4339·97	0·4	36 AU per mm.
4200·03	4199·95	0·4	30 AU per mm.

* Two or three oxygen lines in the neighbourhood of this line may affect the observed value.

SUMMARY.

The experiments have shown :—

(A) That it is possible to observe the first member (4686) of the series

$$\nu = 109750 \left\{ \frac{1}{\left(1\frac{1}{2}\right)^2} - \frac{1}{\left(\frac{n}{2}\right)^2} \right\},$$

which includes the lines given by formulæ (3) and (4), and also a line which agrees in wave-length with the first member (6560·4) of the series

$$\nu = 109750 \left\{ \frac{1}{(2)^2} - \frac{1}{\left(\frac{n}{2}\right)} \right\},$$

which includes the Pickering lines and the lines at 6560·4... predicted by Bohr, in a helium tube giving no trace of the hydrogen lines.

(B) That the experimental values for the wave-lengths of the Pickering lines agree with the theoretical values calculated by Bohr within the limits of experimental error.

These results strongly point to the conclusion that the

series spectrum of hydrogen consists only of lines which are represented by the formula

$$\nu = 109704 \left(\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2} \right),$$

and that the series spectrum of helium in addition to the ordinary helium lines consists of all the lines which are represented by the formula

$$\nu = 109750 \left\{ \frac{1}{\left(\frac{n_1}{2} \right)^2} - \frac{1}{\left(\frac{n_2}{2} \right)^2} \right\}.$$

The author wishes to thank Sir Ernest Rutherford for bringing the subject of the present investigation to his notice and for valuable suggestions and encouragement during the course of the research.

The University of Manchester,
Dec. 1914.

XXXIII. *Simplified Deduction of the Formula from the Theory of Combinations which Planck uses as the Basis of his Radiation Theory.* By P. EHRENFEST and H. KAMERLINGH ONNES [*].

W E refer to the expression

$$C_P^N = \frac{(N-1+P)\,!}{P\,!\,(N-1)\,!}, \quad \cdots \quad (A)$$

which gives the number of ways in which N monochromatic resonators $R_1, R_2, \ldots R_N$ may be distributed over the various degrees of energy, determined by the series of multiples $0, \epsilon, 2\epsilon \ldots$ of the unit energy ϵ, when the resonators together must each time contain the given multiple $P\epsilon$. Two methods of distribution will be called identical, and only then, when the first resonator in the one distribution is at the same grade of energy as the same resonator in the second, and similarly the second, third, ... and the Nth resonator are each at the same energy-grades in the two distributions.

Taking a special example, we shall introduce a symbol for the distribution. Let $N = 4$, and $P = 7$. One of the possible distributions is the following : resonator R_1 has reached the

energy-grade 4ϵ (R_1 contains the energy 4ϵ), R_2 the grade 2ϵ, R_3 the grade 0ϵ (contains no energy), R_4 the grade ϵ. Our symbol will, read from left to right, indicate the energy of R_1, R_2, R_3, R_4, in the distribution chosen, and particularly express that the total energy is 7ϵ. For this case the symbol will be :—

or also more simply :—

With general values of N and P the symbol will contain P times the sign ϵ and $(N-1)$ times the sign $\mathbf{O}$ *. The question now is, how many *different* symbols for the distribution may be formed in the manner indicated above from the given number of ϵ and $\mathbf{O}$? The answer is

$$\frac{(N-1+P)!}{P!(N-1)!} . \qquad \cdots \cdots \quad (1)$$

Proof : first considering the $(N-1+P)$ elements $\epsilon \ldots \epsilon$, $\mathbf{O} \ldots \mathbf{O}$ as so many distinguishable entities, they may be arranged in

$$(N-1+P)! \qquad \cdots \cdots \quad (2)$$

different manners between the ends $\mathbb{I}\,\mathbb{I}$. Next note, that each time

$$(N-1)!\,P! \qquad \cdots \cdots \quad (3)$$

of the combinations thus obtained give the *same* symbol for the distribution (and give the same energy-grade to each resonator), viz. all those combinations which are formed from each other by the permutation of the P elements ϵ† or the $(N-1)$ elements $\mathbf{O}$. The number of the *different* symbols for the distribution and that of the distributions themselves required is thus obtained by dividing (2) by (3) q. e. d.

* We were led to the introduction of the $(N-1)$ partitions between the N resonators in trying to find an explanation of the form $(N-1)!$ in the denominator of (A). Planck proves that the number of distributions must be equal to the number of all " combinations with repetitions of N elements of class P," and for the proof, that this number is given by the expression (A), he refers to the train of reasoning followed in treatises on combinations for this particular case. In these treatises the expression (A) is arrived at by the aid of the device of " transition from n to $n+1$," and this method taken as a whole does not give an insight into the origin of the final expression.

† See Appendix.

APPENDIX.

The contrast between Planck's hypothesis of the energy-grades and Einstein's hypothesis of energy-quanta.

The permutation of the elements ϵ is a purely formal device, just as the permutation of the elements O is. More than once the analogous, equally formal device used by Planck, viz. distribution of P energy-elements over N resonators, has by a misunderstanding been given a physical interpretation, which is absolutely in conflict with Planck's radiation-formula and would lead to Wien's radiation-formula.

As a matter of fact, Planck's energy-elements were in that case almost entirely identified with Einstein's light-quanta, and accordingly it was said that the difference between Planck and Einstein consists herein, that the latter assumes the existence of mutually independent energy-quanta also in empty space, the former only in the interior of matter, in the resonators. The confusion which underlies this view has been more than once pointed out [*]. Einstein really considers P similar quanta, existing *independently of each other*. He discusses, for instance, the case that they distribute themselves irreversibly from a space of N_1 cm.³ over a larger space of N_2 cm.³, and he finds, using Boltzmann's entropy-formula, $S = k \log W$, that this produces a gain of entropy [†]:

$$S - S_0 = k \log \left(\frac{N_2}{N_1} \right)^P , \quad \ldots \quad \ldots \quad (\alpha)$$

i. e. the same increase as in the analogous irreversible distribution of P similar independent gas-molecules, for the number of ways in which P quanta may be distributed, first over N_1, then over N_2 cells in space, are to each other in the ratio

$$N_1^P : N_2^P . \quad \ldots \quad \ldots \quad \ldots \quad (\beta)$$

If with Planck the object were to distribute P mutually independent elements ϵ over N resonators, in passing from N_1 to N_2 resonators the number of possible distributions would in this case also increase in the ratio (β) and correspondingly the entropy according to equation (α). We know,

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[*] P. Ehrenfest, *Ann. d. Phys.* vol. xxxvi. p. 91 (1911) ; G. Krutkow, *Physik. Zschr.* vol. xv. pp. 133, 363 (1914).

[†] A. Einstein, *Ann. d. Phys.* vol. xvii. p. 132 (1905).

however, that Planck obtains the totally different formula

$$\frac{(N_1-1+P)\,!}{(N_1-1)\,!\,P\,!} : \frac{(N_2-1+P)\,!}{(N_2-1)\,!\,P\,!} \quad \cdot \ \cdot \ \cdot \quad (\gamma)$$

(which only corresponds approximately with (β) for very large values of P) and a corresponding law of dependence of the entropy on N. This can be simply explained as follows : Planck does not deal with really mutually free quanta ϵ; the resolution of the multiples of ϵ in separate elements ϵ, which is essential in his method, and the introduction of these separate elements have to be taken *cum grano salis* ; it is simply a formal device entirely analogous to our permutation of the elements ϵ or **O**. The real *object which is counted* remains the number of all the different distributions of N resonators over the energy-grades 0, ϵ, $2\epsilon \ldots$ with a given total energy Pϵ. If, for instance, P$=3$, and N$=2$, Einstein has to distinguish $2^3=8$ ways in which the three (similar) light-quanta A, B, C can be distributed over the space-cells 1, 2.

	A.	B.	C.
I.	1	1	1
II.	1	1	2
III.	1	2	1
IV.	1	2	2
V.	2	1	1
VI.	2	1	2
VII.	2	2	1
VIII.	2	2	2

Planck, on the other hand, must count the three cases II., III., and V. as a single one, for all three express that resonator R_1 is at the grade 2ϵ, R_2 at ϵ ; similarly, he has to reckon the cases IV., VI., and VII. as one ; R_1 has here ϵ and R_2 2ϵ. Adding the two remaining cases I. (R_1 contains 3ϵ, R_2 0ϵ) and II. (R_1 has 0ϵ, R_2 3ϵ), one actually obtains

$$\frac{(N-1+P)\,!}{(N-1)\,!\,P\,!} = \frac{(2-1+3)\,!}{(2-1)\,!\,3\,!} = 4$$

different distributions of the resonators R_1, R_2 over the energy-grades.

We may summarize the above as follows :—Einstein's hypothesis leads necessarily to formula (α) for the entropy and thus necessarily to Wien's radiation-formula, not Planck's. Planck's *formal device* (distribution of P energy-elements ϵ over N resonators) *cannot be interpreted in the sense of Einstein's light-quanta.*

XXXIV. *The Visibility of Radiation.* By P. G. Nutting[*].

THE quantitative relation between light and radiation has long been sought by many investigators. Herschel, exploring the spectrum with a thermometer, found that the radiation continued beyond what was visible. The invisible ultra-violet portions of spectra were long ago explored by photography. Langley[†], twenty-five years ago, explored the infra-red solar spectrum with his fine wire bolometer, and in the visible spectrum measured the amounts of energy of various wave-lengths required for reading print. Pflüger[‡] and König and Dieterici[§] determined the relative amounts of energy required to just produce a luminous sensation in different parts of the spectrum. König[||] continued his investigations from the threshold of vision up to an intensity of about 500 metre candles.

About ten years ago it was clearly recognized that in order to define light in terms of the radiation which excites it, an intermediate function, the visibility of radiation, must be formulated and its constants determined for the average normal eye. Goldhammer[¶], in 1905, partly reduced some of König's data and expressed visibility as a function similar in form to that giving the spectral energy of a perfect radiator. Hertzsprung[**], in 1906, took a rough average of all available threshold data and formulated visibility as a logarithmic hyperbola. The author[††], independently of Goldhammer and Hertzsprung, reduced the data of Langley, Pflüger, and König, and in 1907 published this, a function

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[*] Communicated by the Author.
[†] S. P. Langley, *Am. Journ. Sci.* xxxvi. p. 359 (1888).
[‡] A. Pflüger, *Ann. Ph.* ix. p. 185 (1902).
[§] König and Dieterici, *Zs. Psy. Phys. Sinn.* iv. p. 241 (1893).
[||] A. König, *Ges. Abhandlungen.*
[¶] D. A. Goldhammer, *Ann. Ph.* xvi. p. 621 (1905).
[**] E. Hertzsprung, *Z. Wiss. Phot.* iv. p. 43 (1906).
[††] P. G. Nutting, *Phys. Rev.* xxiv. p. 202 (1907) ; *Bull. Bu. Stds.* v. p. 261 (1908).

representing it, and the related Purkinje effect, and made a rough determination of its principal constant, the maximum ratio of the candle to the watt.

Recently Ives * has applied the flicker photometer to the determination of visibility with excellent results, and has published data for eighteen different subjects in the region from ·48 to ·64μ. I have here to present a similar set of data for twenty-one subjects with extensions of the visibility

Fig. 1.—Diagram of Visibility Apparatus.
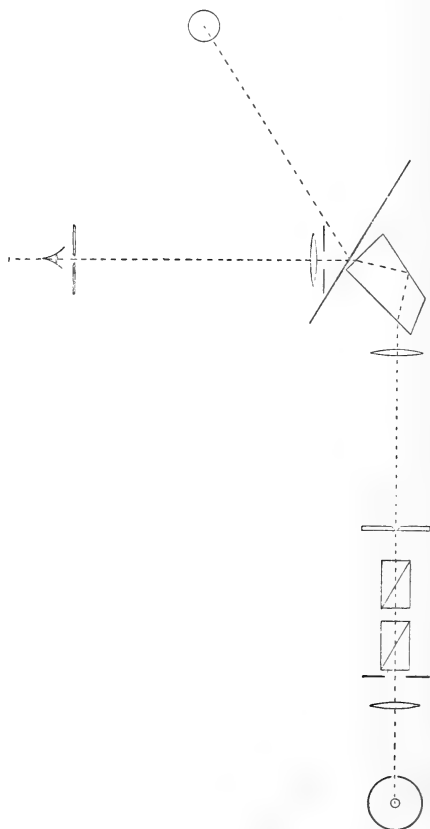
curves farther into the red and violet, and the results of a number of direct determinations of the maximum ratio of the candle to the watt.

* H. E. Ives. Phil. Mag. Dec. 1912. See also Thürmel, *Ann. Ph.* xxxiii. p. 1154 (1910).

The method of determining the visibility curves was similar to that used by Ives. A wave-length spectroscope was fitted with a Whitman disk flicker photometer, so that the pure spectral hue and a white surface illuminated by a standard lamp were viewed alternately (fig. 1).

Instead of a glow lamp as a source we used one of the acetylene standard lamps designed by Dr. Mees, and tested and described recently by Mr. Lloyd Jones [*]. This is essentially a cylindrical flame from a $\frac{1}{4}$ foot Bray tip surrounded by a metal chimney in which is a re-entrant window screening out all but a horizontal section about 5 mm. high. This source is extremely constant in intensity as well as in quality.

Intensities were varied by means of a pair of Nicol prisms before the slit, the slit remaining of constant width, and therefore the spectrum of constant purity.

The observing pupil was 0.57×2.57 mm. throughout, the standard intensity 350 mc. or the equivalent of 241 mc. through a pupil of 1 sq. mm. ; test curves run at twice, $\frac{1}{2}$, $\frac{1}{4}$ and $\frac{1}{16}$ this illumination showed that it was safely outside the range of the Purkinje effect.

The energies representing equal luminosities were determined by placing at the ocular a Rubens bismuth-silver thermopile connected to a Paschen galvanometer, both made by Dr. Coblentz. This gave the spectral energy distribution of acetylene in the spectrum actually observed. As a further check, the dispersion curve of the spectroscope was determined, and the spectral energy computed from the bolometric data of Coblentz and Stewart on acetylene ; the two determinations agreed throughout.

The visibility data obtained are summarised in the following tables. Three independent curves were run by each subject on different days. In combining the curves, ordinates were weighted according to height by reducing to equal areas (equal total light in a constant energy spectrum). In fig. 2 are plotted individual mean visibilities together with the mean of all 21 subjects.

The average visibility curve (fig. 3) for the 21 subjects agrees well with that of previous determinations. It is slightly more contracted than that obtained by Ives, the greatest difference from Ives' mean being on the left (blue) side of the curve near the maximum. The mean wavelength of maximum visibility is ·555 as against ·553 obtained by Ives.

* L. A. Jones, Trans. I. E. S. ix. p. 716 (1914).

Subject.	λ ·49	·50	·52	·53	·54	·55	·56	·57	58	·60	·62	·64	λ max.
L. A. J. ...	·192	·274	·715	·888	1·006	1·042	1·026	·953	·842	·577	·308	·132	·5520
F. A. E. ...	248	350	662	819	910	967	976	934	863	632	351	160	5573
J. R. H. ...	234	367	705	863	952	982	977	924	816	572	334	149	5533
J. I. C.......	196	287	610	787	913	970	975	954	886	673	385	188	5577
J. G. C. ...	304	440	751	855	917	947	946	891	810	562	316	147	5530
H. L. H. ...	237	358	686	811	911	963	965	935	859	626	359	175	5570
V. G. M. ...	146	250	618	794	915	970	986	962	892	669	391	183	5580
L. E. J. ...	223	330	612	766	876	929	946	923	857	673	415	202	5597
L. W. E. ...	221	311	679	841	960	1·010	1·016	959	863	604	335	146	5550
L. M. F. ...	253	370	688	838	934	985	986	942	854	602	322	163	5560
M. B. S. ...	185	293	650	841	972	1·036	1·031	963	829	572	340	223	5547
W. R. F. ...	399	507	796	919	986	1·000	968	888	775	493	247	144	5490
C. W. F. ...	238	313	701	854	944	988	991	955	871	608	323	130	5553
M. B. H. ...	167	255	626	834	963	1·023	1·022	966	870	640	356	173	5550
O. T.	263	367	661	804	924	975	967	918	822	593	393	183	5547
M. L. S. ...	290	369	654	884	1·021	1·072	1·049	958	840	534	270	128	5523
C. E. S. ...	223	305	589	760	904	986	995	964	893	664	394	176	5573
A. McD. ...	138	245	626	794	918	982	990	950	872	676	393	203	5553
S. E. S......	190	300	658	846	972	1·035	1·032	968	850	581	333	138	5550
K. H.	245	372	697	851	932	972	979	942	854	595	333	153	5540
P. G. N. ...	182	273	714	878	996	1·055	1·038	978	845	568	285	136	5532
Average ...	·227	·330	·671	·835	·944	·995	·993	·944	·851	·605	·342	·163	·5550

Fig. 2.—Individual Visibility Curves compared with Mean.
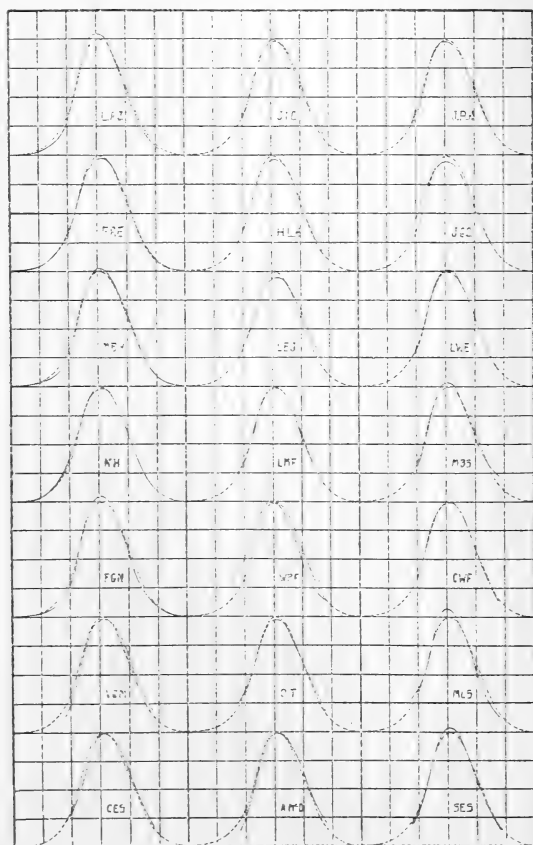
In fig. 3 are included the new data for the violet and extreme red given in the following table (p. 306) for five subjects. These data were obtained by means of the mercury lines 406, 436, 492, 546, and 578, together with helium lines 439, 447, 492, 502, 588, and 568 checked against the acetylene spectrum for energy.

Fig. 3.—Visibility Curves.
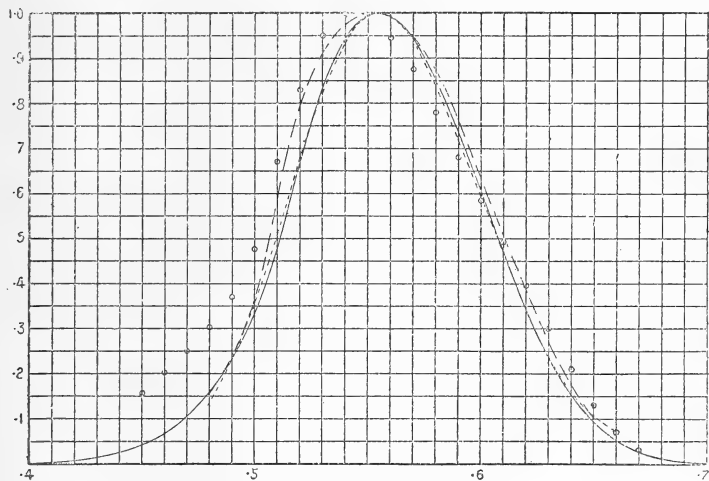
(o o). König's data reduced by Nutting, 1907.
(— —). Ives' mean of 18 subjects.
(——). Author's mean of 21 subjects.
(– – – –). Curve calculated by formula 1.

The theoretical formula whose values are given in the table and plotted in fig. 3, is of the form

$$V = V_m R^a e^{a(1-R)}, \quad \cdots \cdots (1)$$

in which $R = \lambda_{max.}/\lambda$, and $a = 181$. The curve computed for the constants $\lambda_m = 0 \cdot 555$ and $a = 181$ agrees very well with the data of the new mean experimentally determined curve between wave-lengths $\cdot 48$ and $\cdot 65\,\mu$. The departure from the actual curve in the extreme red and violet is of slight consequence in computing the luminosity of sources on account of the relatively low visibility of radiation in those regions.

Complete Data on Five Subjects and Average Curves.

Wave-length (μ).	L.A.J.	F.A.E.	M.B.H.	K.H.	P.G.N.	Mean visibility.	Ives. Mean.	König (N). Mean F.G.H.	Computed from formula.
·400	003	002	002	002	002	002			
·410	005	003	003	003	0·3	003			
·420	008	008	005	004	009	008			
·430	010	014	008	009	013	012	029*		
·440	018	026	014	018	020	023			
·450	031	047	028	037	029	038	047*	158	
·460	055	078	049	068	048	066	073*	201	
·470	089	118	077	112	077	105	107*	250	
·480	129	170	114	171	118	157	154	302	135
·490	184	250	164	254	170	227	235	370	232
·500	274	350	255	372	273	330	363	476	358
·510	489	489	439	544	430	477	596	670	514
·520	715	662	626	697	714	671	794	830	675
·530	888	819	834	851	878	835	912	950	824
·540	1·006	910	963	932	996	944	977	996	933
·550	1·042	967	1·023	972	1·055	995	1·000	990	994
·560	1·026	976	1·022	979	1·038	993	990	945	993
·570	953	934	966	942	978	944	948	875	939
·580	842	865	870	854	845	851	875	780	839
·590	711	760	763	732	709	735	763	630	717
·600	577	632	640	595	568	605	635	585	585
·610	428	488	490	462	402	468	509	492	454
·620	310	354	356	333	285	342	387	336	343
·630	201	237	245	233	196	247	272	300	235
·640	130	157	151	153	136	151	175	210	158
·650	074	099	080	096	087	094	104	128	108
·660	038	058	044	054	051	051	068*	70	072
·670	019	029	023	026	028	028	044*	032	
·680	009	013	012	009	013	012	026*		
·690	004	007	006	004	006	007			
·700	002	002	003	002	002	002			

* Extrapolated

Now the spectral energy of a normal radiator at a temperature T is well represented in the visible spectrum by the Wien-Paschen function

$$E_\lambda = C_1 \lambda^{-n} e^{-C_2/\lambda T}. \quad \ldots \quad \ldots \quad (2)$$

Hence the light emitted by such a radiator will be given by the integral of $EVd\lambda$ from 0 to ∞. Call this integral L, then *

$$L = A\left(\frac{B}{T} + 1\right), \quad \ldots \quad \ldots \quad (3)$$

in which

$$A = C_1 V_m \lambda_m^a \, \Gamma(n+a-1)(a\lambda_m)^{-n-a+1}, \text{ and } B = C_2/a\lambda_m.$$

L has the maximum value

$$L_m = V_m\left(\frac{n-1}{n+a-1}\right)^{\frac{1}{2}}$$

at a temperature

$$T_m = \frac{C_2}{(n-1)\lambda_m}$$

or about 6530 if we take $n = 5$, $a = 181$, and $C_2 = 14500$.

The remaining visibility constant V_m must be determined experimentally. It is the ratio of the candle (or lumen as preferred) to the watt at the wave-length of maximum visibility. The simpler method is to measure in metre candles as light and in watts as energy some given monochromatic illumination, preferably of a wave-length near that of maximum visibility. The first determinations of V_m were made by this method by Dr. Drysdale† and the writer‡ seven years ago. We obtained 16·7 and 13·5 cand./watt respectively, values of the right order of magnitude but much too low on account of stray radiation. More recently, Fabry and Buisson § have made a determination by this method, and obtained the value 55 cand./watt using the green mercury line 5461 from a powerful mercury arc.

The other method for determining V_m is indirect but less subject to large systematic errors, and it gives, under certain conditions, a direct relation between the international candle and the watt. A source of light is used having a continuous spectrum and whose spectral energy distribution is known. With radiometer and photometer, the radiation at a given

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* P. G. Nutting, B. S. Bull. v. p. 305 (1908); vi. p. 337 (1909); 'Applied Optics,' p. 158 (1912).

† C. V. Drysdale, Proc. Roy. Soc. lxxx. p. 19 (1907).

‡ P. G. Nutting, Elec. World, June 26, 1908.

§ Fabry and Buisson, *Compt. Rend.* cliii. p. 254 (1911).

distance in a given direction is determined in metre candles
and in watts per square centimetre ; from these total candles
per watt is found. Then by graphical integration of the
spectral energy and spectral luminosity (energy times visi-
bility) curves, V_m is readily calculated.

For example, suppose that the spectral energy curve has
an area A, while the measured energy is W metre-watts then

$$\int E d\lambda = A = W.$$

Call the area of the spectral luminosity curve B, and suppose
the illumination is C metre candles, when and where the
energy is W metre-watts. Then

$$V_m \int \frac{V}{V_m} E d\lambda = V_m B = C.$$

By division, $V_m = \frac{C}{W} \frac{A}{B}$, hence knowing C/W by direct

determination and A/B by graphical integration, the funda-
mental constant V_m may be readily determined. The pre-
cision attainable by this method depends upon the uncer-
tainties in the three quantities used, (1) relative visibility
V/V_m, (2) the specific quality C/W, and (3) the spectral
energy $E(\lambda)$ of the source used in relative watts per unit
difference in wave-length.

I have recently tried the monochromatic method with
mercury green light and the total spectrum method with
various sources.

Filtered mercury light gave a very low value (4·86 metre-
watts to 12·7 metre candles or $V_m = 2·6$ C/W) in spite of
every precaution to screen out the stray radiation and correct
for the remainder.

Mercury light dispersed with a high intensity spectroscope
gave better results, but the uncertainty is still large owing
to (1) the photometric comparison of pure green with white,
and (2) the removal of the thermopile (or other radiometer)
from the spectroscope to face the energy standard. We
obtained

220 mc.	6·54 mw.	38·6 C/W	J. H.	
215	,,	38·0	N partly rested.	
320	,,	48·9	N rested.	

In measuring the brightness, merely looking at anything
illuminated with mercury light will greatly depress the eye
sensibility to Hg green, while the fatigue caused by adjusting
the mercury lamp persists for perhaps an hour. Even using
a specially designed lamp and every precaution against stray
radiation, I regard the final result as uncertain by 10 per cent.

With the total spectrum method the sources used were

acetylene, pentane, Hefner, Nernst (two efficiencies), tungsten and carbon (three efficiencies). The acetylene source was a Mees standard burner (see above), the pentane and Hefner were primary standard lamps, the Nernst was of Westin house make, 1 03 × 13 mm. filament, the tungsten an old type evacuated lamp, and the carbon of the " gem " type. The quality determinations (means of three to six) are as follows :—

	Observations.		Standard quality.		Mean horizontal.
	M–W.	M–C.	W./C.	C/W.	W/cm.²/C at 1 m.
Hefner	6·84	·871	7·84	·1276	6·24 × 10⁻⁵ watt
Pentane...............	14·2	1·625	8·75	·1144	6 97 ,,
Acetylene	2·45	·731	1·67	·598	1·23 ,,
Nernst ·80 amp. ...	21·96	12·42	1·75	·570	1·29 ,,
,, ·67 ,, ...	13·32	6·46	2·06	·484	1·64 ,,
Tungsten 1·20 W/C.	5·48	4·94	1·11	·903	0·884 ,,
Carbon 4·0............	11·77	2·54	4·64	·216	
,, 3·3............	14·20	4·10	4·12	·243	
,, 2·7............	16·06	4·58	3·51	·286	

In calculating the illumination constant V_m, these quality determinations and the above visibility curve (V/V_m) were used. The required spectral energy curves available were, however, found to be inadequate. Either the visible portion is not known with sufficient precision or else the conditions under which the whole curve was taken is not specified with sufficient detail. After these curves have been freshly determined, for the sources whose luminous quality has been determined, the constant V_m should be determinable to perhaps two or three per cent.

In the case of acetylene, spectral energy determinations by Coblentz (B. S. Bull. vii. pp. 291–3) enable us to evaluate V_m to about 5 per cent. uncertainty. We find for relative integrals of energy and luminosity A/B = 626/5·66 = 110·6. For C/W we obtained 0·598, hence V_m = 66·2 candles per watt. The uncertainty arises from the uncertainty in the " saturation " of the infra-red part of the radiation for the thickness of flame used. I hope soon to have a number of more precise values of V_m.

I am greatly indebted to friends in the Photographic and Chemical divisions as well as to colleagues in the Physics division, who so cheerfully served as subjects in obtaining visibility data. I am particularly indebted to Mr. Felix Elliott, who recorded and reduced nearly all of the thousands of observations.

Research Laboratory,
    Eastman Kodak Co.
        Rochester, N.Y., July 1914.

XXXV. *The Gyroscopic Theory of Atoms and Molecules* [*].
By ALBERT C. CREHORE [†].

IN obtaining the equilibrium positions of two atoms as they unite to form a molecule, it was shown in a former paper [‡] that the distance between the atoms is great compared with the radius of the orbits of their electrons, probably more than a thousand times as great. The order of magnitude of the radii of the orbits of the electrons in the atoms was there estimated as 10^{-12} cm. [§] This result follows from the better known molecular dimensions and the calculated ratio between molecular dimensions and the radii of the orbits. Following this conception, certain modifications as to the distribution of the electrons within the positive electricity are suggested, not only to introduce the quanta of Planck but also to account for both the X-ray spectra recently published by Moseley and luminous spectra.

The present tendency among atomic theorists is to favour with Rutherford an atom with a central positive nucleus having electrons circulating in orbits large compared with the radius of the nucleus. One reason for favouring this atom is that it explains the observed scattering of the alpha particles in their passage through matter. Another reason is that it accounts for the large mass of an atom, as compared with that of an electron, by the small radius of the positive electricity, the mass of the hydrogen atom being about 1900 times that of the electron. The theory involves the

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[*] Since this paper was communicated the work of calculating the forces between any two atoms of the nature described in the text has been in progress. The integral equations have been obtained when the axes of the atoms lie in one plane, either parallel to each other in the same or in opposite directions, or perpendicular to each other. These equations enable us to specify the directions of the axes of the atoms in a cubic crystal such as rock-salt or potassium chloride, and to show that the whole crystal is a very stable arrangement. The distances between the atoms agree with those calculated by Prof. Bragg within the limits of error. The experimental work on crystals seems to be a confirmation of the theory advanced in this paper, because the same fundamental values here given of the size of the positive electricity and the speed of revolution of the electrons in the atom have enabled us to construct theoretically a crystal such as rock-salt, and to obtain the same distances as found experimentally.

The derivation of the forces between two atoms and the proof that these atoms may form a stable crystalline structure of dimensions agreeing with the experimental determinations, forms the subject of a future communication.

[†] Communicated by the Author.
[‡] A. C. Crehore, Phil. Mag. July 1913, p. 25.
[§] *Loc. cit.* p. 56.

principle that when an electrical charge is in motion, it possesses an apparent mass that increases with the velocity, and implies that all mass is due to this electromagnetic origin. For high velocities, one-tenth or more of that of light, experimental measurements show an agreement with this theory. The suggestion has been made that perhaps this electromagnetic mass constitutes the whole of the mass, and we do not, therefore, need to assume anything else. It is probable that the velocities of the electrons in the atoms are of an order of 1/700 that of light, and to apply the above result to them extends the law far beyond the range of experimental evidence. The theory is, moreover, usually applied to the positive electricity in the atom which is supposed to be relatively at rest, a condition as far removed as possible from the experimental observation. It requires that as neutral atoms grow heavier with the addition of electrons, the positive nucleus must grow rapidly larger in radius to show increasing mass, the radius being directly proportional to the number of electrons or to the mass, unless some supposition is introduced which prevents the positive electricity from amalgamating as it were, and preserves the individual positive electrons so that their radii are not changed, and the mass is increased by the additional numbers of them. If this is the case, it is difficult to understand the nature of the forces that hold them together, and I am not aware that any definite hypothesis on this point has ever been suggested. That some such thing must be the case seems to be required by the experimental fact that when an atom breaks up in radioactive transformations, atoms of helium are given off, each containing an exact multiple of the smallest positive charge. On the whole, this conception that the principal mass is due to that substance which fills the smallest volume, and that the radius varies directly with the mass or number of electrons, is very unnatural. This makes the volume eight times as much for double the mass.

On the theory here advanced, the mass of the atom is shown to be proportional to the volume of the positive electricity. This volume is first determined by independent means, and when compared with the approximate volume of the electron, the ratio is the same as the ratio between the masses of the atom and the mass of electrons composing it, about 1900. On this theory the mass per unit volume everywhere, whether of positive or of negative electricity, at slow velocities is the same and is constant, approximately equal to 10^{12} grams per cubic centimetre, as is shown in a subsequent section.

The distance 10^{-8} cm. is sometimes referred to as of the order of atomic dimensions. This seems unfortunate, because it implies that this is the approximate size of atoms. This distance, obtained from the kinetic theory of gases, means that the atoms in collision approach each other to within about this average distance before rebounding, thus behaving as though they are of this size. On the present conception of atoms, it is the magnetic and electric fields accompanying and surrounding them which determine this distance of rebound, and in one sense this is the effective size of the atom. In another and more rational sense, the size of the atom is determined by the size of the orbits of the electrons composing it, and in this theory of the atom these are of the order of 10^{-12} cm., from one to ten thousand times smaller than the so-called atomic dimensions.

It will aid in the discussion to point out the characteristic features of this corpuscular-ring gyroscopic theory of the atom, not only because the small absolute dimensions of the atom have altered the whole case, but because the ascendency of the central nucleus theory has deterred many from serious consideration of another form of atom. The small magnitude of the electron orbits alters the case again, because the electron, with a radius of the order of 10^{-13} cm., is not of a negligible size compared with the distances between electrons in the same atom. Even if the law of repulsion between them is the same as for electric charges as we know them in the gross, there is no reason for applying the inverse square law of repulsion to the electrons within the atom, which at such distances does not hold for two charged spheres. The law of repulsion may not be different for single electrons and for aggregates of them, but in discarding the inverse square law the equilibrium figures originally calculated by Thomson using this law are greatly modified.

In this theory, the volume of the positive electricity is supposed to increase by a fixed amount with the addition of each electron. This fixed increment in volume is the volume of the smallest positive portion, or unit of electricity, having a charge equal to and a volume larger than the electron. It may be called the positive electron. The volume of this elementary positive unit may be found by dividing the volume of the positive electricity of any neutral atom by the number of electrons it contains. There is just the same difficulty here connected with the positive electricity as there is in the central nucleus atom referred to in regard to the amalgamation of the different positive electrons, and no

hypothesis is now introduced to permit of the positive electricity again separating into definite fixed units when the atom breaks up. It seems necessary to do this sometime. Using the dimensions of the atom obtained in the previous paper[*], the volume of the positive electron comes out $2 \cdot 7 \times 10^{-36}$ cu. cm., corresponding to a radius of $\cdot 86 \times 10^{-12}$ cm. if taken as spherical.

The Number of Electrons per Gram of any Substance Constant.

On any atomic theory, the number of electrons per **atom** is approximately proportional to, and Rutherford makes it one half of, the atomic weight. It seems as if there is reason, from a comparison with the periodic table of the elements, to take the number of electrons as about equal to the atomic weight, but proportionality alone is sufficient to show that the number of electrons per gram for all substances is nearly constant. If the electrons per atom are equal to the approximate atomic weight, then the number per gram must be about 6×10^{23}, the so-called gram-molecule constant, which thereby assumes a very definite physical meaning.

If the number of electrons per gram is constant, then it follows on this theory that the volume filled by all the atoms in a gram is also constant, since the vast majority of atoms are neutral, and each electron is accompanied with positive electricity having a fixed volume. It is possible, then, to find the total volume of all the atoms in a gram, because it is the same as the total volume of positive electricity in all the atoms, the electrons being contained within the volume of the positive electricity. It is found by multiplying the constant 6×10^{23} by the volume of the unit positive electricity $2 \cdot 7 \times 10^{-36}$ cu. cm., which gives $1 \cdot 62 \times 10^{-12}$ cu. cm. Disregarding the fraction and taking the order of magnitude as 10^{-12} cu. cm., this constant expresses the volume of all the atoms in a gram of any kind of substance. If, for example, a gram of water which ordinarily fills one cubic centimetre could be compressed until its atoms are brought into contact, or until all interspace between atoms is eliminated, it would fill only 10^{-12} instead of one cubic centimetre. Or again, if 10^{12} grams of water, normally filling a space of 10^{12} cu. cm., which is the volume of a cube one hundred metres on a side, is similarly compressed until there is no interspace between its atoms, it would only fill one cubic centimetre.

[*] *Loc. cit.* p. 56.

The spaces between the atoms on this theory are vast compared with the total volume of the atoms themselves, but, as before stated, this gives a somewhat false conception of this atom. The electric and magnetic fields surrounding each and extending to relatively great distances in a sense determine the size of the atom. But, on the other hand, the volume filled by the atoms themseves as above considered is important. If we regard the æther as a continuum with a uniform density everywhere, and consider that the positive and the negative electricity are really portions of it differentiated from the rest merely by possessing different energy characteristics in some way not now specified, the volume filled by the atoms in a gram gives a definite meaning to the term æther density. The density should be the reciprocal of the volume of the atoms per gram, namely 10^{12}. We have just seen that, as far as density is concerned, we can make 10^{12} grams of matter out of one cubic centimetre of the æther, assuming the density of the positive electricity to be the same as the rest of the æther. An analogous case would be to think of a large portion of the cosmos filled with stars and compare its density regarded as matter with that of the Earth. The filmy structure of the cosmos compared with the Earth would be analogous to that of ordinary matter compared with the æther. This conception is not new, but the very close coincidence of the volume, 10^{-12} cu. cm., of all the atoms in one gram as calculated from this theory with the well-known reciprocal of the number 10^{12}, which those who have taken this view of the æther have accepted as the approximate value of its density, is very significant.

We shall take 10^{12} as the value of the æther density, and reversing the process indicated, determine from it the size of the unit positive electricity or positive electron taken as a sphere. It comes out $\cdot735 \times 10^{-12}$ cm. radius instead of $\cdot86$ as above.

On Mass.

If there are 6×10^{23} electrons in every gram of any substance, and the single electron atom is that of hydrogen, then the mass of the hydrogen atom is $\dfrac{1}{6 \times 10^{23}} = \cdot166 \times 10^{-23}$ gram. Taking the mass of the electron as $\cdot878 \times 10^{-27}$ gram, the ratio of the masses of the hydrogen atom to that of the electron is 1900. The radius of the positive electron as above determined is $\cdot735 \times 10^{-12}$ cm., and a sphere having a radius of $\cdot593 \times 10^{-13}$ cm. has a volume 1/1900 of the positive electron. Taking this latter figure as the size of

the electron, it then appears that the mass of every atom is proportional to the volume of the electricity in that atom, and that both the positive and the negative electricity have the same mass per unit of volume, that is the mass is 10^{12} grams per cubic centimetre, the value of the æther density.

Beta Particles from Radioactive Substances.

A certain difficulty has arisen in the central nucleus atomic theory in explaining the beta particles from radioactive matter. It seems certain * that the beta particles in radioactive transformations cannot come from a ring whose radius is comparable with 10^{-8} cm. For this reason those who advocate the Rutherford atom with electron orbits of a size calculated by Bohr †, are forced to restrict the source of the beta particles to the electrons which emanate from the very inside rings or the nucleus itself. On the author's theory this difficulty vanishes, and any electron may give rise to the beta particle as far as the size of the orbit is concerned, because all orbits in neutral atoms are sufficiently small, being of the order of 10^{-12} cm. radius.

The positions of the electrons outside of the nucleus in the Rutherford atom have been estimated by Bohr by making use of the conception of quanta, and Planck's universal constant " h." Whatever the explanation of quanta may be, it is now very generally admitted that they have a real physical existence, and no atomic theory can ignore the fact. It is just as possible on this new theory of the atom as with the central nucleus atom to recognize the quantum of Planck.

In this paper some of the older features of the corpuscular ring theory are retained, but the whole is modified in certain important particulars. The retained features are, first, that the electrons are within the mass of the positive electricity and are confined approximately to one plane, the enormous frequency of orbital revolution being sufficient cause to restrict them to this plane. Second, the positions in this plane are chiefly determined, as in the old theory, by the electrostatic and magnetic forces, but with these differences, that the forces of repulsion no longer obey the inverse square law on account of the near approach of the electrons to each other, and that the existence of quanta also modifies the equilibrium positions, somewhat changing the radii of the rings in a manner to be described.

* J. W. Nicholson, Phil. Mag. April 1914, p. 544.
† N. Bohr, Phil. Mag. September 1913, p. 488.

From these premises alone certain important conclusions, which are in harmony with experimental observations, follow almost axiomatically. In neutral atoms, as electrons are added forming increasingly heavier elements, and as the positive electricity increases in volume by a fixed amount for each electron, retaining an approximately spherical shape, it results that the diameter of the rings lying in a plane must increase at a greater rate than the diameter of the corresponding positive electricity, since the latter increases nearly as the cube root of the number of electrons and the former at a greater rate, somewhere between the first power and the square root of the same number. There must, then, come a time when, as electrons are added, the diameter of the outside ring equals that of the positive electricity. No more electrons than this can be accommodated within the positive electricity, and there is, therefore, a superior limit to atomic weights. As nearly as can be estimated, this point is reached for that number of electrons which corresponds to the element uranium, the heaviest of the elements, and it is not surprising that there are no heavier atoms found. In these heavier atoms the outside ring is most unstable, and comparatively slight forces may drive an electron outside of the positive electricity, where the law of force suddenly changes allowing it to escape. It seems natural on this view to expect to find self-radioactive elements at the latter end of the periodic table, and in fact we come to uranium, thorium, radium, radium emanation, etc., all self-radioactive elements. The degree of radioactivity should not follow precisely this order, as will be evident when the irregularities introduced by the equilibrium positions are taken into account.

Scattering of the Alpha Particles.

The scattering of the alpha particles may be explained by this form of atom as well as by the central nucleus atom. A study of the electric and magnetic fields surrounding a single atom of this kind shows that it is possible for an alpha particle to pass straight through the atomic field without deviation or to be reflected at any possible angle. The deviation depends upon the relative directions of the axes of rotation of the atom and of the approaching atom, and upon the direction of the line of approach. The forces may be either attractive or repulsive according to circumstances. While no quantitative proof is here given of the precise law of scattering, it must be conceded that the known laws of scattering supply

no argument against this atomic conception. The immense difficulties of obtaining the desired positive proof will be evident to anyone who attempts it. The introduction of the magnetic forces with the conception of polarity in addition to the electrostatic forces is the source of the difficulty.

X-ray Spectra.

It seems as if the discovery of Prof. Laue [*] of a method of measuring the frequencies of the X-rays by the use of crystals is destined to give experimental measurements which will eventually provide a complete working atomic theory. I have endeavoured to account on this theory of the atom for the series of X-ray spectra as determined by Moseley [†], and have worked out a distribution of the electrons within the positive electricity to account for his two principal series, the $K\alpha$ and the $L\alpha$. Moseley has given the general equation

$$\nu = A(N - b)^2 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

as representing approximately the experimental measurements, where ν is the frequency of the X-rays, A and b are constants for a given series, and N is an integer, being a series of ordinals increasing by unity from element to element. This equation gives a straight line by taking $\nu^{\frac{1}{2}}$ as abscissa and N as ordinate, and may be written

$$N = a\nu^{\frac{1}{2}} + b \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where A is replaced by $1/a^{\frac{1}{2}}$.

The manner of finding the possible positions of the electrons to give both the observed X-ray and the light spectra in this form of atom may be something like the following. It is first assumed in common with other theories that there is no radiation of energy when the orbits of the electrons are circular and the motion is in the steady state at a fixed angular velocity. It is the disturbance of this state only which gives rise to the radiation or absorption of energy. It is also assumed that the angular moment of momentum of each electron in every atom is the same and is constant, that is

$$m\omega r_n^2 = k_1^2, \text{ a constant}, . \quad . \quad . \quad . \quad . \quad (3)$$

where m is the mass, ω the angular velocity in the orbit, and r_n the radius of the orbit of the ring of n electrons. If s is

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[*] Laue, Friedrich, and Knipping, *Münch. Ber.* pp. 303–322 (1912).

[†] H. G. J. Moseley, *Phil. Mag.* Dec. 1913, p. 1024; April 1914, p. 703.

the frequency of revolution of each electron in its orbit, then $\omega = 2\pi s$.

Any disturbance of the uniform state of motion due to outside causes will in general disturb the planes of the orbits of the electrons as well as their eccentricities, and thereby give rise to motions similar to those of gyroscopes but more complex. It is suggested that the resulting rapid nutations, both natural and forced, cause the high frequencies of the X-rays, and that the slow precessional motions cause the light spectra. The difficulties of any complete investigation compel me to resort to the analogy of the gyroscope, the investigation of which is known. In the case of a simple gyroscope with a rigid wheel, acted upon by an external moment of force M, the frequency of the resulting nutations is given by the expression

$$\nu = \frac{C\omega}{2\pi A}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

where ω is the angular velocity of the wheel, and C its moment of inertia about the principal axis, and A its moment of inertia about an axis in the plane of the wheel. If we now conceive of the mass of a single electron as uniformly distributed like a ring throughout its entire orbit, then the moment of inertia C about the principal axis is double A, the moment about an axis in the plane of the ring. Hence, $C/A = 2$, and

$$\nu = 2s. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (5)$$

That is to say, the frequency of nutation of the electron in the single electron atom is twice its frequency of revolution. Moreover, this frequency is independent of the external disturbing force, though the energy is not, and is dependent only upon the constitution of the atom itself. This shows that the order of magnitude of X-ray frequencies, if due to this cause, is not different from the frequency of revolution of the electron in its orbit.

When the number of electrons in a ring is more than one, the analogy to the rigid wheel can hardly be used to give even an approximation to the principal nutation frequencies. We shall make the assumption that the frequency of the nutations occurring in a ring of n electrons is proportional to the number of electrons, n, in the ring and is equal to

$$\nu = k_2 n. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (6)$$

Comparing this with the equation (3) we derive the relation

$$\frac{v r_n^2}{n} = k^2 \text{ a constant.} \quad \ldots \quad (7)$$

Or

$$v^{\frac{1}{2}} = k \frac{n^{\frac{1}{2}}}{r_n} = kx, \quad \ldots \quad (8)$$

where x replaces $n^{\frac{1}{2}}/r_n$, and is proportional to the square root of the frequency of the X-rays. The corpuscular ring theory gives the approximate values for both n, the electrons per ring, and r_n, the radius of the ring, and hence values of x proportional to the square root of the frequencies. Charting these values points are obtained, as we pass across a series of elements in the periodic table, which have some semblance to the straight line series of Moseley. However, it is necessary to restrict this to the $K\alpha$ series which applies to the lighter elements, as the number of electrons corresponding to Zr, the first of the $L\alpha$ series, is too large to handle. The best line to represent the $K\alpha$ series when projected back to the ordinal axis intersects at about three units instead of unity as Moseley takes it, making $b = 3$ instead of $b = 1$ in equation (1). Rydberg * makes this constant exactly 3 in his revision of the Moseley ordinals, and has in doing this added 2 to each ordinal in the series of elements, making N for aluminium 15 instead of 13. In deriving the spectra in this paper, Rydberg's interpretation of the Moseley ordinals is used.

The next process is to abandon the approximate values of the radii r_n obtained from considerations of equilibrium and proceed to calculate them on the basis of Moseley's observations, assuming the points to lie exactly upon his $K\alpha$ line or series. In so doing, we are at liberty to distribute the electrons in rings in any manner, but that particular arangement has been chosen which is demanded by the periodic system. The resulting arrangement, therefore, contains an explanation of both the periodic system of the elements and the X-ray series of Moseley.

In fig. 1, the line I represents the $K\alpha$ series, the marks upon it being the spectrum lines experimentally obtained, but it begins at $N = 3$, and the abscissæ are proportional but not equal to the square root of the frequency, being equal to $x = \frac{n^{\frac{1}{2}}}{r_n}$. The first point on the line at $N = 15$ and $x = 1.875 \times 10^{12}$ is found by taking Al to be the configuration $27 = 3, 9, 15$, there being 27 electrons total with an outside

* J. R. Rydberg, Phil. Mag. July 1914, p. 147.

ring of 15. Taking the volume of the unit of positive electricity in absolute dimensions as above obtained, a fair approximation to the absolute radius of the outside ring can be made. Having thus found two points on the line representing this series, its position is determined. It is to be

Fig. 1.

$$x = \sqrt{\nu}/k$$
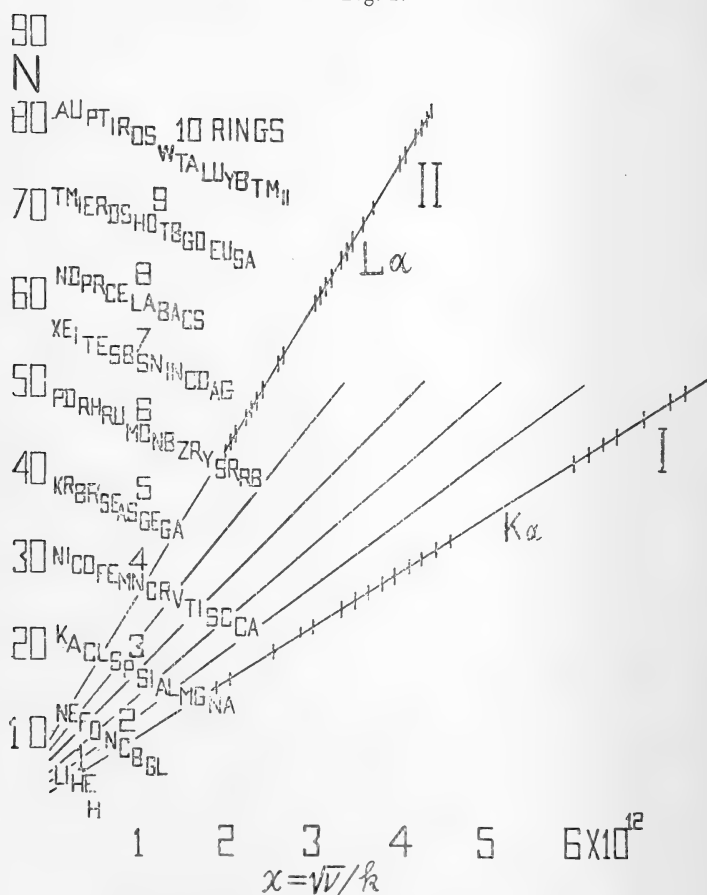
noticed that all the spectrum lines in this series are **not** caused by the outside ring of electrons. Al, Si, and P are attributed to the outside ring; S, Cl, and A to the second ring; K, Ca, Sc, and Ti to the third ring; V, Cr, Mn, Fe, and Co to the fourth ring; Ni. Cu, Zn, Ga, Ge, As, Se, and Br to the fifth ring; Kr, Rb, Sr, Y, Zr, Nb. Mo, and possibly a few more to the sixth ring. In a similar manner

the Lα series, which is represented by the line II in the figure, begins at Zr with a line due to the outside ring, and for a few of the elements in this region, which have lines in each series in Moseley's table, the one is due to the first and the other to the sixth ring of electrons.

If this mode of explaining the observed X-ray spectra is correct, it is conjectured that several other series of lines between the Kα and the Lα exist. Of course a determination of the spectra on this theory depends entirely upon the accurate determination of the frequencies of nutation of the electrons in their orbits—a most difficult problem—but the simple assumption made above that $\nu = k_2 n$ points to a distribution of the electrons in good agreement with the corpuscular ring theory. There is no doubt that the complete solution of these frequencies of nutation is more complex than the assumption made; and even if this is one solution, it is not surprising that Moseley has observed several other series of varying intensity lying close to these principal series.

A way of approximating to the absolute value of the frequencies is by the use of Planck's constant. The energy required to separate to a great distance an electron from the unit of positive electricity may be taken as the minimum energy change that ever takes place. If the electron starts from the surface of the sphere of radius $b = \cdot735 \times 10^{-12}$ cm. as above determined, it is shown to be $e^2/2b$. Equating this to hs, where s is the frequency of revolution and h is Planck's constant, we obtain

$$hs = \frac{e^2}{2b} = 15\cdot5 \times 10^{-8} \quad . \quad . \quad . \quad . \quad (9)$$

where $e = 4\cdot77 \times 10^{-10}$, and $h = 6\cdot5 \times 10^{-27}$. Hence for the single electron atom, which on this theory is taken to represent hydrogen, the frequency of revolution of the electron is *

$$\left. \begin{array}{l} s = 2\cdot385 \times 10^{19}, \\ \nu = 2s = 4\cdot770 \times 10^{19}. \end{array} \right\} \quad . \quad . \quad . \quad (10)$$

and

On the equilibrium theory, when there are two electrons, they place themselves halfway from centre to circumference of the positive sphere, and with only one electron it would go to the centre, making the radius in the first case $\cdot46 \times {}^{-12}$ cm., and in the second case zero. The supposition that the angular moment of momentum is constant for all electrons and not zero, indicates that the true value

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* The letter ν is reserved for the nutation frequencies and s is introduced for frequencies of revolution.

of r_1 lies probably between these limits. The value $r_1 = \cdot 285 \times 10^{-12}$ cm. has been chosen by an inspection of the curve of radii for the atoms having 2, 3, 4, and 5 electrons, it being assumed that these radii are the least affected by the equal moment of momentum hypothesis. It must be regarded as a rough approximation at best, but the results that follow from it seem to be in close accord with the distances between atoms as experimentally determined.

Since the publication of the experimental equilibrium figures obtained by electrostatically charged spheres * suspended as pendulums in which the maximum number of electrons was 20, an experimental series obtained with magnets floating on water up to 75 magnets has been published †. It is shown that the groups repeat themselves periodically around the central groupings shown in fig. 2, which accounts well for the periodic system of the elements.

Fig. 2.

Fig. 3 represents the atoms of the first nine series of the periodic table according to these groupings. The outside circle represents the boundary of the positive electricity on the assumption of spherical shape, and the numerous small black dots represent in magnitude the relative size of the electrons. The number of electrons per ring is indicated by the numbers in the lower left corner of each square, the Rydberg ordinals in the lower right corner, and the symbol for the element in the upper left corner. The radii of the rings where electrons are shown are derived from fig. 1, and this arrangement gives on this theory the X-ray spectra of Moseley. Where certain rings are omitted, as, for example, in chlorine, their radii are not obtainable from fig. 1. In chlorine the ring of 6 and the single electron are omitted because the lines lie to the right of the Kα series.

Light Spectra.

One of the pertinent criticisms that may be made against any atomic theory is that it has not accounted for the observed luminous spectra of the elements. Although Bohr has in a brilliant manner given an explanation of some of

* *Loc. cit.* Plate II.
† E. R. Lyon, Phys. Rev., March 1914, p. 232.

Fig. 3.

the series of spectral lines, notably those of H and He, yet it may fairly be said that luminous spectra have not been explained by any atomic theory. Nicholson [*] has shown in a seemingly conclusive manner that these spectra are not really accounted for on Bohr's hypothesis. It is not surprising that it is difficult to account for light spectra, but it should not be inferred that there is not sufficient basis in this theory for a possible explanation. The range of X-ray frequencies is from 1,000 to 10,000 or more times greater than the frequencies of light, and it becomes necessary to find periods of a comparatively low order of magnitude. An estimate of the values of these slower or luminous frequencies in the theoretical atom containing a single electron and representing hydrogen is given below, but it is evident that there must be many periods of a low order in more complex atoms that are not easily specified. Each atom must in fact be considered as a little gyroscope having several rings or wheels of very great but different periods of rotation. If the axis of rotation is disturbed by any cause certain nutations and precessions will necessarily occur.

In the theory of the ordinary gyroscope having a rigid wheel there are two classes of periods due to the action of external forces, the frequencies of the one being independent of the external forces, and of the other dependent upon them. If the gas giving the spectrum consists of individual atoms, as may be the case with He, then these periods caused by external forces may be of the first class and have constant values whatever the outside disturbing force may be, they being determined solely by the properties of the atom itself. If the gas consists almost entirely of molecules of more than one atom, then additional periods of a fixed value should be obtained because of the constant effect of the atoms upon one another. The gyroscopic theory of these atoms is much more intricate than that of a rigid wheel. There is a flexible rather than a rigid connexion between the electrons, and it is necessary to have a more definite knowledge of the cause which gives rise to the existence of quanta, or which holds each electron to a constant angular moment of momentum, if this is a fact.

Our theory has enabled us to make a complete specification of the hydrogen atom consisting of one electron within the positive electricity, determining the volume of the positive electricity, the radius of the orbit, and the frequency of revolution of the electron, as well as the relative positions of

* J. W. Nicholson, Phil. Mag. July 1914, p. 90.

the two hydrogen atoms which form the diatomic molecule, including their distance apart, and the angle of latitude that the line joining their centres makes with the planes of their orbits. Although it is the average value of the forces when taken over a long time that determines the stable position of equilibrium of the two atoms forming the molecule, yet the instantaneous values of the forces on the individual parts of the atom varying during one revolution give rise to the precessional motion which causes the light spectra. We will now determine in absolute dimensions the distances referred to, and then proceed to calculate for this simple molecule the precessional period or frequency which gives rise to the light spectrum of hydrogen.

The Hydrogen Molecule.

The mechanical force that two hydrogen atoms, having a single electron each, exert upon one another when their axes are parallel and in the same direction, may be derived from equations (42) * and (44) of the former paper. They show that two such atoms come to stable equilibrium with each other when their axes are in the same straight line, the revolution of the electrons being in the same direction, the phase angle between them being zero, so that the line joining the electrons is always parallel to the line joining the centres of their orbits. When the distance between the centres of the atoms is

$$\chi = \frac{\sqrt{3}}{2\pi} \frac{c}{s} = \cdot 347 \times 10^{-9} \,\text{cm.}, \quad \ldots \quad (11)$$

where c is the velocity of light and s the frequency of orbital revolution of the electron obtained from Planck's constant in (10), then it has been found that the atoms are in stable equilibrium with each other.

It is to be noticed that the distance between the two hydrogen atoms is very small compared, for instance, with the distance between a sodium and a chlorine atom in rock-salt, which is $2 \cdot 814 \times 10^{-8}$ cm.; $81 \cdot 2$ times smaller, and yet the same values of the fundamental constants s and r_1 serve to show that we get an equilibrium distance of this larger order when the sodium and chlorine atoms are used. This

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* In giving the coefficients $B_{2,2}$, $B_{4,2}$, &c., middle of page 70, Phil. Mag. July 1913, a column of B's was omitted. The first column should read $B_{2,2} = \frac{3}{2}$; $B_{4,2} = 5B_{2,2}$; $B_{6,2} = \frac{7}{5}B_{4,2}$; $B_{8,2} = \frac{9}{3}B_{6,2}$; $B_{10,2} = \frac{11}{4}B_{8,2}$; $B_{12,2} = \frac{13}{5}B_{10,2}$; $B_{14,2} = \frac{15}{6}B_{12,2}$.

peculiarity of the hydrogen atom will later serve to explain some of the compounds into which hydrogen enters.

A small displacement in any direction whatever from this position of equilibrium as origin gives rise to a restoring force directed toward this origin. For small displacements the restoring force is proportional to the displacement, giving rise to harmonic vibrations about this point or origin. The restoring force per unit of distance and per unit of mass along the line joining centres of the atoms is

$$F_a = -\frac{4}{3^{\frac{3}{2}}}\frac{e^2\beta^5}{a^3}, \quad \ldots \quad (12)$$

where a is the radius of the orbit of the electron and e its charge, and β the velocity of the electron divided by that of light. If we equate this force to the mass times the acceleration per unit of distance, we find the frequency of oscillation in the direction of the line joining centres to be

$$n_a = \frac{e\beta^{\frac{5}{2}}}{3^{\frac{3}{4}}\pi m^{\frac{1}{2}}a^{\frac{3}{2}}}, \quad \ldots \quad (13)$$

where m denotes the mass.

The restoring force per unit of distance and mass along any line perpendicular to the line joining centres is

$$F_p = -\frac{2}{3^{\frac{3}{2}}}\frac{e^2\beta^5}{a^3}, \quad \ldots \quad (14)$$

exactly one half the force in (12) along the line of centres. The corresponding frequency of oscillation along the perpendicular line is, therefore,

$$n_p = \frac{n_a}{2^{\frac{1}{2}}}. \quad \ldots \quad (15)$$

If we consider that the mass which is subjected to this force is that of the single electron in the atom, we obtain in numerical values taking $e = 4 \cdot 77 \times 10^{-10}$; $a = \cdot 285 \times 10^{-12}$; $m = \cdot 878 \times 10^{-27}$; $\beta = 2\pi sa/c$; $s = 2 \cdot 385 \times 10^{19}$; $c = 3 \times 10^{10}$,

$$\begin{aligned} n_a &= 1 \cdot 12 \times 10^{15} \\ n_p &= \cdot 79 \times 10^{15} \end{aligned} \Big\} \quad \ldots \quad (16)$$

The wave-lengths of light corresponding to these frequencies are

$$\begin{aligned} \lambda_a &= 2680 \times 10^{-8} \text{ cm. along,} \\ \lambda_p &= 3800 \times 10^{-8} \text{ cm. perpendicular} \end{aligned} \Big\} \quad \ldots \quad (17)$$

If we consider that the mass which is subjected to this force is that of the positive electron in the atom, we obtain in numerical values taking $m = 1·66 \times 10^{-24}$ and other quantities as above,

$$\left.\begin{array}{l} n_a = ·026 \times 10^{15} \\ n_p = ·018 \times 10^{15} \end{array}\right\} \quad \cdots \quad (18)$$

The wave-lengths of light corresponding to these vibrations are

$$\left.\begin{array}{l} \lambda_a = 117000 \times 10^{-8} \text{ cm.,} \\ \lambda_p = 165000 \times 10^{-8} \text{ cm.} \end{array}\right\} \quad \cdots \quad (19)$$

The light spectrum of hydrogen is not to be attributed to these two simple vibrations of the electron alone (16) and (17), but rather to the disturbances to which they give rise in the motion of the single electron in its orbit.

It is remarkable that this calculated value of the frequency of the electron perpendicular to the line joining centres comes so close to the experimental value of the fundamental constant in Balmer's series of hydrogen lines. The wavelengths in Balmer's series * of hydrogen lines are given by the equation

$$\lambda = 3647·20 \times 10^{-8} \frac{m^2}{m^2 - 4}, \quad \cdots \quad (20)$$

m being a series of integers.

If we express Balmer's series in terms of the frequency instead of the wave-length, (20) may be written

$$n = b + \frac{a}{m^2}, \quad \cdots \quad (21)$$

where

$$b = \frac{c}{3647·20 \times 10^{-8}} = ·823 \times 10^{15}, \text{ and } a = -4b = -3·292 \times 10^{15}.$$

It has been shown that this law of Balmer's can be derived † from considerations of ordinary dynamics provided there is a proper sort of gyroscopic connexion between the two atoms. Let u and v be scalar functions of the time and of the position of points in the two atoms respectively at an

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* J. S. Ames, Phil. Mag. vol. xxx. p. 55 (1890).
† E. T. Whittaker, Proc. Roy. Soc. ser. A. vol. lxxxv. No. A 578, June 9, 1911, p. 262. The importance of this demonstration warrants repeating in full, as given in the original paper, since we have shown that the values are obtainable from the hydrogen atom.

angle θ such that the potential energy of the one atom is represented by

$$\tfrac{1}{2}au^2 + \tfrac{1}{2}b\left(\frac{\partial u}{\partial \theta}\right)^2,$$

and of the other by

$$\tfrac{1}{2}av^2 + \tfrac{1}{2}b\left(\frac{\partial v}{\partial \theta}\right)^2,$$

where a and b are constants. Then if the gyroscopic connexion between the atoms gives rise to a term $\dfrac{\partial u}{\partial \theta} \cdot \dfrac{\partial^2 v}{\partial t\, \partial \theta}$ in the kinetic potential, the equations of motion are

$$au - b\frac{\partial^2 u}{\partial \theta^2} - \frac{\partial^3 v}{\partial t\, \partial \theta^2} = 0,$$

$$av - b\frac{\partial^2 v}{\partial \theta^2} + \frac{\partial^3 u}{\partial t\, \partial \theta^2} = 0.$$

If, now, u and v are assumed to be simple periodic functions given by the equations

$$u = A \sin (nt + m\theta),$$
$$v = B \cos (nt + m\theta),$$

where m denotes an integer and n gives the frequency, the solution of these equations gives

$$(a + m^2 b)A = m^2 n B,$$
$$(a + m^2 b)B = m^2 n A;$$

whence eliminating A and B, we obtain Balmer's equation for the frequency as in (21) above,

$$\pm n = b + \frac{a}{m^2}.$$

The low-frequency vibrations and the long wave-lengths due to the vibration of the positive electron in (20) and (21) may be considered as heat rather than light. When the energy of these vibrations becomes excessive the whole atom may depart so far from the equilibrium position that it will not return to it and the substance becomes volatilized by excessive heating.

Photo-Electric Phenomena.

There are certain experimental facts connected with the photo-electric effect which are not easily explained on any atomic theory. It seems as if this theory contains elements which will eventually lead to a more complete understanding

of these phenomena. When ordinary light falls upon a body under the proper conditions electrons are emitted. The velocity of each electron emitted is independent of the intensity, but depends directly upon the frequency of the light. The number of emitted electrons depends upon the light energy or intensity, but the velocity of the individual electron does not. The slightest change in the frequency of the light produces a corresponding change in the emitted velocity, and the velocity is a continuous function of the frequency. No form of atom which is only capable of resonance at particular fixed frequencies peculiar to itself would be capable of such response to external forces. The gyroscopic nature of the atom, however, renders it capable of responding to the frequency of the impressed force. An analogous case is to be found in the precessional motion of the earth due to the comparatively slow revolution of the sun or the moon in an orbit inclined to the plane of the equator, so that the gyroscopic couple acting upon the earth varies with the position of the sun or moon. It is well known that this produces a periodic motion of the earth's axis corresponding to twice the frequency of the orbital revolution of the sun or moon. There is, similarly, produced in each atom upon which the light falls a frequency double that of the light.
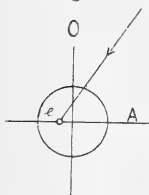
Let fig. 4 represent the single electron atom upon which light is falling in the direction indicated. If we imagine that the light produces a pressure upon the electron, perhaps in just the way that it produces a pressure upon any small particles, then this pressure will vary harmonically with the time corresponding with the frequency of the light. This is a very low frequency compared with that of the electron in its orbit, and it will produce a precession of the pole of the orbit having twice the frequency of the impressed force, the light pressure.

Fig. 4.

The energy so received from the light may accumulate until an electron escapes. This is likely to happen always at a critical velocity which is fixed by the character of the atom rather than the intensity of the light and so not vary with the light intensity. The energy, however, is abstracted from the light. A greater light energy merely brings an increasing number of electrons up to the critical point where they quit the atom. A calculation of the manner in which the electron may be ejected, especially in a complex atom, is not undertaken at present, involved as it is with the intricate precessional motions of the electrons. We are

fortunate to be able to show with some degree of probability that this form of atom contains the potentiality, which may some time be more fully realized, of explaining these experimental observations.

Synopsis.

1. The number of electrons per gram of any substance is approximately constant. This follows from any atomic theory which makes the number of electrons per atom proportional to the atomic weight. If the electrons per atom are approximately equal to the atomic weight, as in this theory, then the well-known gram-molecule constant 6×10^{23} is equal to the number of electrons per gram of any substance. Since, in neutral atoms, a positive electron having a fixed volume accompanies each electron, it follows that the volume of all the positive electricity in a gram is also constant. This volume is found by multiplying the volume of the unit positive electron by the number, 6×10^{23}, of electrons per gram. In a previous paper the volume and radius of the positive electron were determined in absolute dimensions, $2 \cdot 7 \times 10^{-36}$ cu.cm., or $\cdot 86 \times 10^{-12}$ cm. radius. Multiplying this volume by 6×10^{23} gives $1 \cdot 62 \times 10^{-12}$ cu.cm. as the volume of all the atoms in a gram of any substance, the electrons being within the positive electricity. The coincidence of this volume per gram with the reciprocal of the quantity 10^{12}, which those who have taken this view of the æther consider represents its density, is very significant. Working in the reverse way from the æther density as a basis, the radius of the positive electron comes out $\cdot 735 \times 10^{-12}$ cm. Taking the radius of the electron as $\cdot 593 \times 10^{-13}$ cm., the volume of the positive electron is 1900 times that of the electron. The mass of the atom is accounted for by the larger volume of the positive electricity, the ratio of the volume of the positive to the negative electricity being the ratio of the masses of the hydrogen atom to the electron. On this view the mass of positive or of negative electricity is the same for equal volumes, equal to 10^{12} grams per cu.cm., the æther density, and the mass of any piece of matter may be calculated in grams by multiplying the volume filled by all its atoms by 10^{12}.

2. Beta particles in radioactive transformations may come from any electron in the atom, since the order of magnitude of the electron orbits is 10^{-12} cm. In the central nucleus theory they cannot come from the outside rings, and must be restricted to the inner electrons or the nucleus itself.

3. The theory shows that a limit of atomic weights should

be reached when the number of electrons is so great that the outside ring, which grows at a greater rate, equals in diameter the positive electricity, which point should occur somewhere near the element uranium. Self-radioactivity is attributed to the fact that when near this limit the outside ring of electrons is most unstable; and comparatively slight forces may drive an electron outside the positive electricity, where the law of force changes allowing it to escape, thus breaking up the figure and requiring readjustment. The self-radioactive elements should, according to this, occur at the latter end of the periodic system, as they do.

4. There is assumed to be no radiation of energy from an atom when the electrons describe circular orbits in the steady state. A disturbance of this state may give rise to rapid nutations of the electrons both natural and forced, accounting for the X-rays. In the single electron or hydrogen atom the natural nutation frequency is twice the frequency of orbital revolution. The orbital frequency is determined from Planck's constant together with the size of the hydrogen atom to be $s = 2.385 \times 10^{19}$, and the characteristic X-ray frequency for hydrogen should, therefore, be twice this value.

5. When there is more than one electron in the same orbit the natural nutation frequencies are not easily obtained from analogy with gyroscopic equations, and an assumption is made that these frequencies are $(\nu = k_2 n)$ proportional to the number of electrons per ring. Upon this assumption, together with the grouping of electrons in rings to represent the periodic table of the elements, a tentative distribution of electrons is given, which would account for the Kα and Lα series of X-ray spectra of Moseley.

6. The comparatively low frequencies of light are attributed to the precessional frequencies of the electrons in their orbits. A calculation of the simplest case, that of the single electron atom, is made to determine the frequency that the one atom in the hydrogen diatomic molecule causes in the other atom. The hydrogen molecule is first determined definitely, including the distance between the two atoms and the angle that their two axes make with the line joining centres. This distance is 1220 times the radius of the orbit of the electron in the atom, equal to $\cdot347 \times 10^{-9}$ cm., and the angle is 0°. The frequency of vibration of the electron in a direction perpendicular to the line joining centres agrees well with the principal constant in the equation expressing Balmer's hydrogen series. It has been shown by Whittaker that if there are certain terms in the differential equations

representing the gyroscopic connexion between the two atoms, Balmer's law may be accounted for, and the demonstration is considered of sufficient importance to repeat in full.

The frequency of vibration of the positive electron in the atom is 43·55 times slower than that of the negative electron, giving long waves which may be considered as heat radiation.

7. This atom is capable of response to any frequency of light, because there are precessional frequencies produced in the atom proportional to those of the impressed force. No form of atom capable of resonance at fixed frequencies only can possibly account for the experimental facts connected with the photo-electric effect. It is suggested that light pressure upon the electron, when the light falls at an angle with the plane of the orbit, is responsible for inducing a precessional variation of double the light frequency.

XXXVI. *On the Series Spectrum of Hydrogen and the Structure of the Atom.*

To the Editors of the Philosophical Magazine.

Gentlemen,—

IN the January number of this magazine Dr. H. Stanley Allen has published two interesting papers in which he considers the effect on the series spectrum of an element if the central nucleus of the Rutherford atom has, besides its electric charge, the properties also of a small magnet. In the first paper, it is shown that a nuclear magnet under certain assumptions might give rise to a number of different series of lines, instead of the single series of lines to be expected if the nucleus consists simply of a point charge. It is shown, however, that a magnetic field of the order of magnitude which may be assumed to occur in the actual atoms will be much too small to account for the different series of lines which have been observed in the spectra of the elements. In the second paper, the formulæ deduced in the first are applied to the hydrogen spectrum, and it is attempted by the help of the hypothesis of a nuclear magnet to explain the very small deviations from the Balmer law which have been observed by Mr. Curtis in his recent accurate measurements of the wave-length of the hydrogen lines. The moment of the nuclear magnet is found to be approximately equal to that of 5 magnetons. The importance of this result, if correct, is easily seen ; but it would appear that some of the deductions made by Dr. Allen are difficult to justify.

The application of the quantum theory in the calculation of the effect of a magnetic field affords a very intricate problem, since there are several possible ways of applying the theory and each of them leads to different results. The only guide on this question seems to be experiments on the Zeeman effect. In the first place, it might be argued as a serious objection against the method of calculation applied by Dr. Allen, that an analogous calculation in the case of a homogeneous magnetic field does not give results in agreement with measurements of the Zeeman effect. I shall not, however, try here to discuss this difficult and unsolved problem *, but will only consider the way in which the formulæ obtained in the first paper are applied in the second paper to the hydrogen spectrum. In this application new assumptions are involved, one of which seems hardly consistent with the main principles of the theory. According to Dr. Allen's calculations, the presence of a nuclear magnet leads to a splitting up of the lines in components situated symmetrically with respect to the original lines, at any rate if the square of the magnetic force is neglected. This result, in itself, will not explain Mr. Curtis's observation, which consists in a small systematical deviation of the "centre of gravity" of the hydrogen lines from the position calculated by the Balmer law†. In comparing the theory with experiments, Dr. Allen now uses only one of the two components calculated. For this, apparently, no explanation is offered; it might, however, be justified by assuming that the nucleus, on account of its small moment of inertia, will always take a position such that its magnetic axes will coincide with the direction of the magnetic force due to the rotating electron. In order to obtain an expression for the frequency of the same type as the empirical formulæ by which Mr. Curtis has represented his results, Dr. Allen next assumes that the correction in one of the terms of his formula can be neglected. This assumption amounts to the neglect of the correction due to the nuclear magnet in one of the "stationary states" of the atom. It seems very difficult to see how this assumption can be justified; for if the nucleus is assumed to be a small magnet, it would appear necessary to have the same magnetic properties for all the states of the atom. According to the theory, these states differ only in the size of the orbit of the rotating electron. If the correction

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* In the special case of a homogeneous magnetic field the problem in question is considered in some detail by K. Herzfeld (*Phys. Zeitschr.* xv. p. 193, 1914) and by the present writer (Phil. Mag. xxvii. p. 506, 1914).

† W. E. Curtis, Proc. Roy. Soc., A, xc. p. 614 (1914).

is not neglected, Dr. Allen's formula will show a deviation
from the Balmer law which is much larger than that observed
by Mr. Curtis, and which has the opposite sign.   It therefore
seems to me that the interesting suggestion of the nuclear
magnet and the calculation of its moment can hardly be
considered as supported by the experiments of Mr. Curtis.

I should like here to draw attention to an effect of
another kind, which involves a correction in the theoretical
formulæ for the hydrogen spectrum, *i. e.* the variation of
the mass of the electron with velocity.   It seems necessary
to take this into account even if other effects may be in-
volved at the same time.   Assuming that the orbit of the
electron is circular, and proceeding in exactly the same way
as that followed in the deduction of the Balmer formula on
the quantum theory, but replacing the expressions for the
energy and the momentum of the electron by those deduced
on the theory of relativity, we obtain the following formula
for the hydrogen spectrum :

$$\nu = \frac{2\pi^2 e^4 m \mathrm{M}}{h^3 (m + \mathrm{M})} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \left[1 + \frac{\pi^2 e^4}{c^2 h^2} \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right) \right],$$

where *e* and *m* are the charge and the mass of the electron,
M the mass of the nucleus, *h* Planck's constant, and *c* the
velocity of light.   In the formula, terms are neglected which
involve higher power than the second of the ratio between
the velocity of the electron and the velocity of light.   The
correction due to the last factor in this formula has the same
sign as the deviations from the Balmer law observed by
Mr. Curtis [*].   However, it accounts only for $\frac{1}{3}$ of the
deviations observed.

In connexion with this discussion it may be remarked that
it seems hardly justifiable to compare the measurement of
Mr. Curtis with any theoretical formula unless the observed
doubling of the hydrogen lines is taken into account.   Con-
sidering that the distance between the components is much
greater than the deviations from the Balmer law and that
the components are of unequal intensity, it is difficult to
know, in the absence of a theoretical explanation of the
doubling, the interpretation to be placed on measurements
of the " centre of gravity" of the lines.   In a previous
paper I suggested that possibly the lines were not true
doublets, but that the doubling observed was produced by
the electric field in the discharge.   As Mr. Curtis points
out, this suggestion does not seem consistent with the

* In the diagram in Mr. Curtis's paper (*loc. cit.* p. 615) the curve
corresponding to an expression of the above type is inadvertently drawn
with its curvature downwards instead of upwards.

observed ratio of the distance between the components of H_a and H_β. It seems also difficult to reconcile with the observed unequal intensity of the components. It may be mentioned here that there is perhaps another way of explaining the observed doubling without introducing new assumptions as to a complicated internal structure of the hydrogen nucleus. For small velocities of the electron, the calculation gives the same result whether the orbits are assumed to be circular or not ; but taking the variation of the mass into account, it can be shown that for higher velocities the orbits will not be stationary unless they are circular. In other cases the orbit will rotate round an axis through the nucleus and perpendicular to the plane of the orbit, in much the same way as if the atom were placed in a magnetic field. It might therefore be supposed that we would obtain a doubling of the lines if the orbits are not circular. The frequency of this rotation of the orbit will depend on the degree of excentricity. For very small alterations from the circular orbit the ratio between the frequency of rotation of the orbit and the frequency of revolution of the electron is given by $\dfrac{2\pi^2 e^4}{n^2 c^2 h^2}$, which for $n=2$ is of the same order of magnitude as the doubling of the hydrogen lines observed. In view, however, of the great number of new assumptions involved in such calculations, it seems to be of very little use to consider this question in detail until more accurate measurements of the distance between the components and especially of its variation for the different hydrogen lines have been made.

I hope in a later paper to deal more fully with some of the problems briefly considered here, and to discuss in some detail the main principles involved in the application of the quantum theory to the problem of series spectra and the structure of the atom.

<div align="right">Yours faithfully,
N. BOHR.</div>

University, Manchester,
    January 12th, 1915.

XXXVII. *Notices respecting New Books.*

The Theory of Relativity. L. SILBERSTEIN, Ph.D. Pp. viii + 295. Macmillan & Co. Ltd. : London, 1914. Price 10s. net.

THIS book is founded on a course of lectures delivered at University College, London ; but the exposition has been made more systematical and has been largely extended so as to include all the most important aspects of the subject. The most

important feature of the book is the attempt to make the subject as real as possible by an examination of the experimental data which are the main foundation of it. In most of the expositions of the theory of relativity this experimental foundation is almost lost sight of in the array of mathematical equations which, in some quarters at any rate, seem to be the only vital thing. We still meet with people who imagine that the whole of mechanics is a series of deductions from Newton's Law of Motion; and that in the exposition of mechanics no appeal is necessary to experiment. The same might have been said of the pre-Newtonian principles which experiment has shown to be erroneous. The same fascination for general principles led Einstein himself to forsake earlier methods and to enunciate two general principles from which all deductions were to be made. Dr. Silberstein is careful to sketch the historical development of the subject from Maxwell, through Hertz, Heaviside and Lorentz, to the final enunciation of his fundamental principles by Einstein. In this sketch he is equally careful to explain the part which the appeal to experiment has taken. The result is that this presentation of the theory has a real look about it, in contradistinction to those expositions which are carried away by the fascination of the universalisation of the application to moving bodies of a set of equations which were primarily put forward to apply only to bodies at rest. The fact is that without the result of Michelson and Morley's experiment there would be no justification for the theory at all. It is because it gives the most direct explanation of their null result and is at the same time not at variance with any other experimental fact, that the theory may claim serious consideration. So much does the reviewer feel this to be true that he would go further, and declare that it will only be when further experimental data of a crucial kind are obtained that the theory will run much chance of becoming definitely accepted as scientific knowledge.

Meanwhile it is necessary that the consequences of the theory should be examined in detail; for by doing this, information may be gained of the kind of way in which further appeal to experiment may be made. It is with this object in view that we would recommend the present volume to be studied.

With regard to the mathematical methods adopted, we may point out that most use is made of quaternionic formulæ; but these are fully explained : so that no one need be deterred on this account. Some use is also made of the matrix method of representation employed by Minkowski.

It must not be thought that Dr. Silberstein is merely an expositor of other people's work. The whole book savours of originality, and no one who wishes to be abreast of this revolutionary subject can afford to leave the book on one side.

It is beautifully printed and appears to be very free from typographical errors.

FIG. 1 a.
λ : 5461
H = 15500

FIG. 1 b.
λ : 4359
H = 15500

P+4 P-3 P+2   P-2 P-3 P-4   P0 P-1 P+1 P0   P+3 P+2 P-2 P-3   P+1 P-1 P+1 P-1

(s)   (p)   (s)   (p

FIG. 2 a.

P+1 P-1   P+1 P-1

(p)

(s)

P-2 P-3 P+3 P+2

H = 6300

FIG. 2 b.

P+1 P-1   P+1 P-1

(p)

(s)

P+3 P+2 P-2 P-3

H = 14600

FIG. 2 c.

P+3 P-2 P-2 P-3 P+3 P+2 P+2 P-3   P+1   P-1 P+1   P-1

(s)   H = 20300   (p)
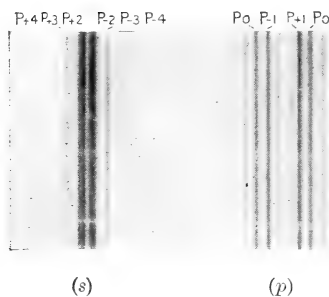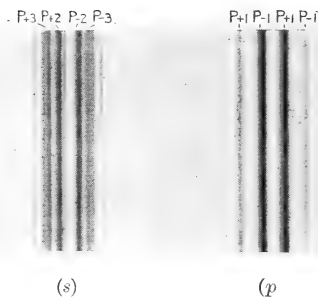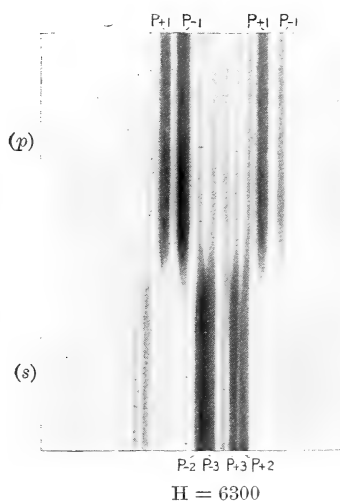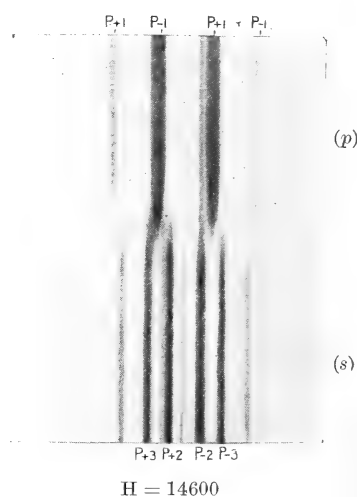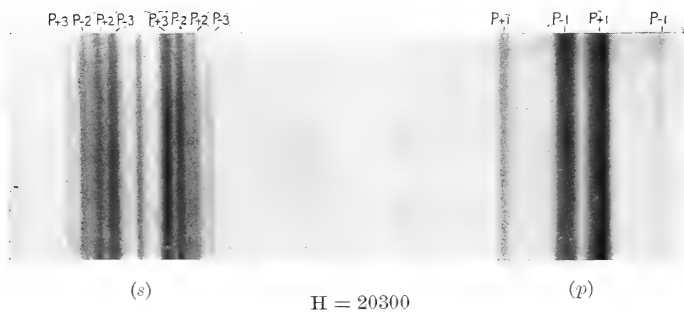
Fig. 3 a.

P_{+1} P_{-1}

Heterogeneous Field.
H : 8700 to 17000.

(s) (p)

Fig. 3 b.

P_{-3} P_{+3} P_{+2} P_{-2} P_{-3} P_{+3}

P_{+1} P_{-1} P_{+1} P_{-1}

(s)

Heterogeneous Field.
H : 9500 to 15000.

(p)

Fig. 7.   4359

p-components.
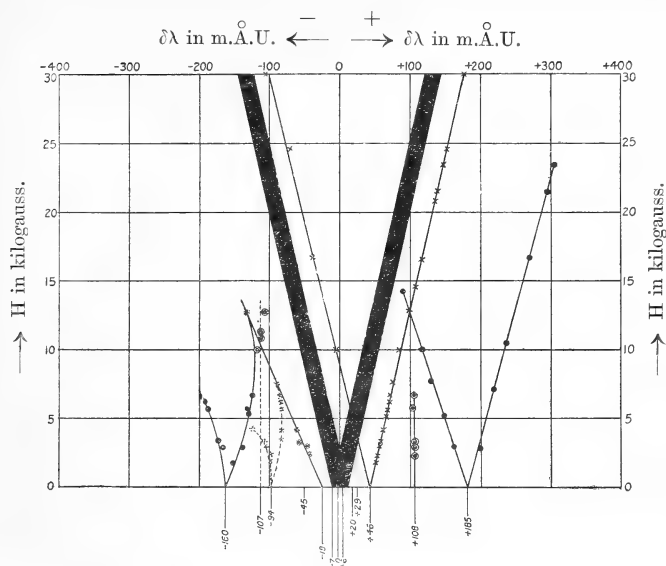
Fig. 8.

s-components.
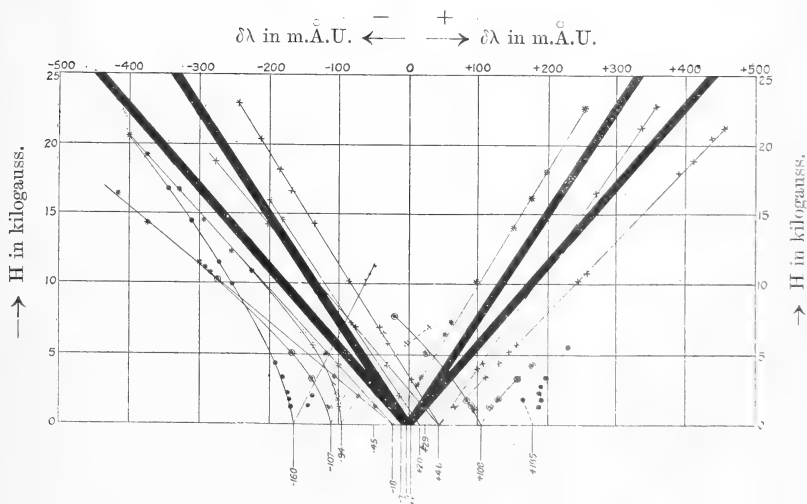
FIG. 1.
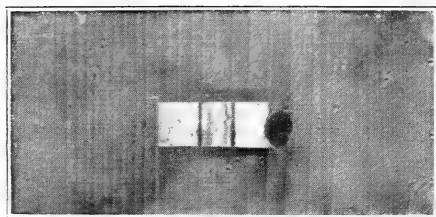
FIG. 2.
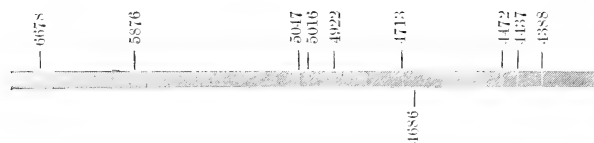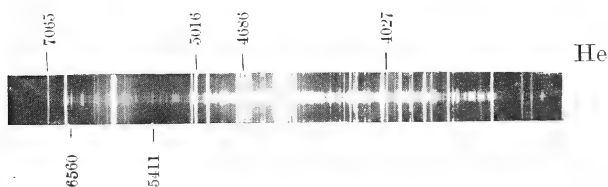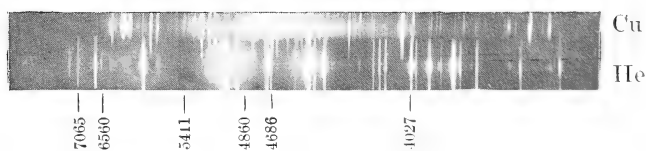
XXXVIII. *The Condensation of Thorium and Radium Emanations.* *By* ALEXANDER FLECK, *B.Sc.*[*]

A LARGE number of experiments have been made on the temperature of condensation and other properties of these emanations. As a result of their first experiments, Rutherford and Soddy [†] found that they were condensed at the same temperature, but more precise measurements made them conclude that while radium emanation condensed at $-155°$ C., thorium emanation, on the other hand, was condensed over a range of temperature varying from $-120°$ C. to $-155°$ C. The well-known experimental facts concerning the chemical non-separability of certain groups of radio-elements from one another and from certain common elements have received a theoretical explanation by the generalization of Russell, Fajans and Soddy, governing the evolution of the radio-elements through the Periodic Table. The elements which appear to be chemically identical occupy the same place in the Periodic Table and are termed "isotopic" elements. The three radioactive emanations are isotopic but, as they belong to the family of chemically inert gases, they are, of course, chemically indistinguishable. Professor Soddy suggested that it would be of interest to examine whether the thorium and radium emanations could be separated from one another by condensation, or whether, as suggested by the work of Sir J. J. Thomson and Ashton

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[*] Communicated by Professor F. Soddy, F.R.S.

[†] Rutherford and Soddy, Phil. Mag. [6] v. p. 561 (1903).
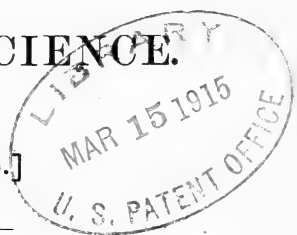
on neon and metaneon, they would have the same temperature of condensation *.

In a paper communicated to Section A of the British Association meeting in Birmingham, September 1913, Ashton brought forward evidence to show that atmospheric neon consisted of two elements of different atomic weight. These two gases could not be separated from one another by means of fractional condensation, but the separation could be effected by diffusion. The atomic weight of the new gas was found by the positive ray method to be 22.

Experiments at Atmospheric Pressure.

The difference found by Rutherford and Soddy in the behaviour of the two emanations when subjected to low temperatures is definite enough, but it has to be remembered that the concentration of radium emanation required to produce a given ionization effect must be approximately 6000 times the concentration of thorium emanation to produce the same effect. The only possible way therefore to test whether the two emanations have exactly the same condensation point, is to have them thoroughly mixed before being cooled to the low temperature. The methods used in the first series of experiments were the same in principle as those used by Rutherford and Soddy, in which the emanation was mixed with air at atmospheric pressure. The apparatus finally used is shown in figure 1. An 80 feet gas-cylinder, A, was used which was in direct connexion with a glass T-piece, B, the vertical limb of which dipped below the water in the glass jar. There were two marks on the stem of the T-piece, M_1 and M_2, and the level of the water in the jar was kept at M_1 whilst the level of the water in the tube was adjusted, by altering the pressure of the escaping gas, to M_2. Immediately beyond the T-piece was a short length of capillary tube, C, so that by maintaining a constant pressure at B, the amount of gas passing through C was directly proportional to the time. The capillary tube was followed by a tube containing phosphorus pentoxide, and then by a piece of wide tube containing the source of thorium emanation. This was a strong preparation of radio-thorium which had been separated from a mixture of radium and mesothorium. Gas coming through the apparatus was therefore mixed with a constant quantity of thorium emanation after the equilibrium amount of emanation had been removed. Beyond the active preparation was a three-way tap, one limb of which went directly to the outer

* Soddy, 'Chemistry of the Radio-Elements,' pt. ii. p. 36.

atmosphere, while the other was connected to a copper spiral made of tube of an internal diameter of 2 millimetres. The end of the spiral was also connected to the outer atmosphere.

Fig. 1.
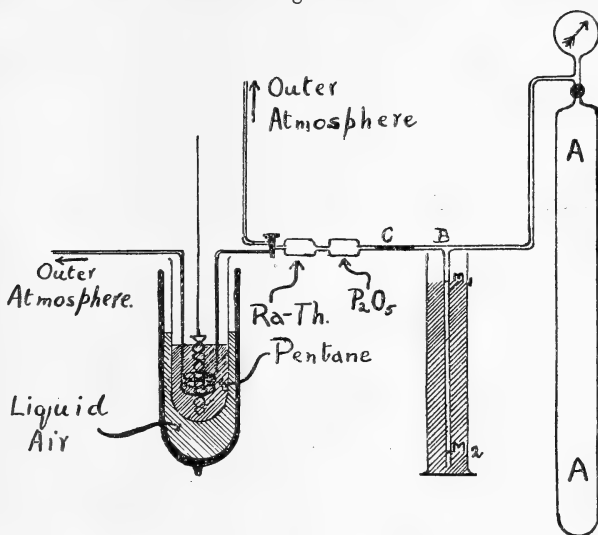
In the hollow of the spiral there was a vertical stirrer driven by an electric motor, and the whole was enclosed by a wide test-tube which contained pentane, cooled externally by liquid air. The temperature was measured by a previously calibrated iron-eureka couple, the hot junction being kept at the temperature of melting ice.

Thorium Emanation alone.—The first experiments that were made were with thorium emanation alone. Air was pumped into A with the help of the liquid air machine until the pressure was equivalent to that of 10 atmospheres. A constant air-stream of 60 c.c. per minute was maintained across the radio-thorium, the gas being sent direct to the atmosphere, while the temperature of the pentane was adjusted to some constant value. When the temperature had been fixed, the air containing thorium emanation was then diverted through the copper spiral and allowed to flow for 40 minutes. The gas-stream was then stopped, the coil removed from the bath and its γ activity measured until the thorium active deposit had attained its maximum after, approximately, three and a half hours. The experiment was repeated, using a fresh coil, for an immersion at liquid air temperature, and, again, with the coil maintained at room temperature for the

standard time.   The small activity obtained by this last
measurement was deducted from all measurements taken at
low temperatures.   The fraction f of the emanation con-
densed is therefore given by the expression

$$f = \frac{A_T - A_R}{A_L - A_R}, \quad \cdots \quad \cdots \quad (1)$$

where A_T, A_L, and A_R are respectively the activities obtained
for immersions of a coil at some low temperature T, liquid
air, and room temperatures.   The curve obtained by plotting
the fraction condensed against the temperature is shown
(figure 2, Curve A), and from it, it is evident that the

Fig. 2.
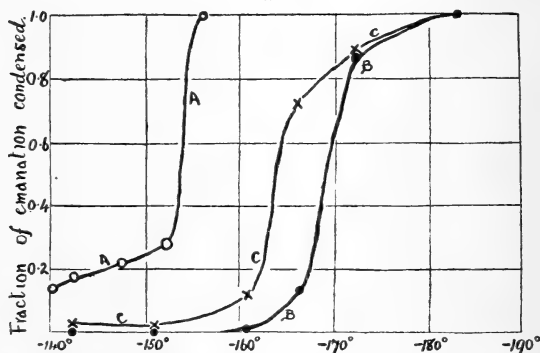
Curve A. Thorium emanation alone.
Curves B and C. Mixed emanations: B, radium; C, thorium.

thorium emanation is gradually condensed until about
$-154°$ C., at which temperature it becomes completely
condensed.

Mixed Thorium and Radium Emanations. — The object
of this preliminary experiment having been attained, the
experiment with the mixed radium and thorium emanations
was proceeded with.   The iron cylinder was exhausted and
14 millicuries of radium emanation introduced, after which
the pressure was again raised to 10 atmospheres.   The
cylinder was allowed to stand over night to ensure complete
diffusion of the emanation, and the experiment carried out
the following day.   In this experiment, the current of air
carrying emanation was 100 c.c. per minute, and the time of
exposure was again 40 minutes at the given temperature.
After the exposure, the temperature of the coil was lowered
to that of liquid air and kept there for $3\frac{1}{2}$ hours, *i. e.* until

the radium active deposit had come into equilibrium with the condensed emanation and the thorium active deposit had reached its maximum activity. The coil was then warmed, and the radium emanation in it displaced by a stream of fresh air. γ-ray measurements were immediately commenced and continued for at least three hours, after which the activity obtained is solely due to thorium active deposit. By multiplying this quantity by the factor 1·119 the value of the maximum activity of the thorium active deposit is obtained. When this latter quantity is subtracted from the initial activity, the remainder gives the effect due to radium emanation alone. The experiment is repeated, of course, for liquid air and room temperatures, and the fraction of the emanation condensed, both in the case of radium as well as of thorium, is obtained by substituting in expression (1). The experiments for the points shown in the curves were carried out in the course of a few hours, so that the radium emanation had not materially decayed while they were in progress.

Curve B (figure 2) is that obtained for the condensation of radium emanation, and curve C that for thorium emanation.

It is seen that the two curves are quite distinct, thorium emanation being apparently more easily condensed than the radium emanation. It has to be noticed, however, that the form of the two curves is the same, while Rutherford and Soddy found that when tested separately their shapes were different. It has also to be observed that the speed of the gas-stream influences the position of the condensation curve, in the case of thorium the curve is displaced to the right by increasing the amount of gas passing through the coil per minute. It is thus evident that the exact temperature at which the emanations condense depends to a large extent on the physical conditions prevailing during the experiment.

There must also be considered the effect of the vapour pressures of the condensed emanations. It is well known that even at the temperature of liquid air, radium emanation has an appreciable vapour-pressure, and we can assume that thorium emanation will likewise have that property. In the case of radium emanation the vapour phase will be continually swept away, while in the case of thorium the condensed emanation quickly changes into the active deposit which remains. Assuming for the moment that the two emanations have the same condensing point, there would be found relatively more thorium active deposit than radium active deposit. Consequently the thorium emanation would

appear to be more easily condensed than the radium. The above results are therefore not a proof that the two emanations have dissimilar properties of condensation.

Experiments at Low Pressures with Radium Emanation.

It was then decided to experiment on the emanations in llosed tubes to avoid sweeping away the vapour phase. The main idea of the method was to have the emanations enclosed in a tube at very low pressure and to assume that a quantity of gas would diffuse throughout the tube instantaneously. This assumption was proved to be correct by experiments that will be described later.

As no work on the condensation of the emanations at low pressures has previously been done, it was thought advisable to work, in the first place, with the single emanations.

Apparatus.—For this experiment, the apparatus and position of electroscopes is shown in figure 3. A lead

Fig. 3.
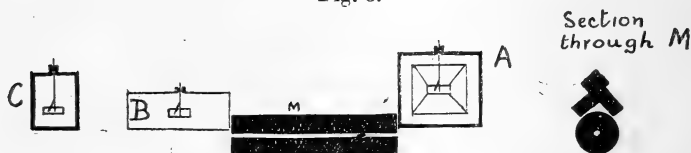
cylinder, M, 44 cm. long and 11 cm. diameter, with a hole 2 cm. diameter bored along its axis was used, and it had on top three lead bars of length equal to that of the lead cylinder and each of cross-sectional area of 25 sq. cm. On the right-hand side was a large sensitive γ-ray electroscope, A, while on the left-hand side were (1) the very sensitive β-ray electroscope, B, described by Soddy[*] in a recent paper, and (2) the small γ-ray electroscope, C. The electroscopes were arranged to be slightly above the axis of the lead cylinder, so that if a radioactive tube was in its centre, no rays except those from any portion of the tube purposely exposed could reach an electroscope without passing through considerable thicknesses of lead. The object of this arrangement was that experiments could be started with a large quantity of radium emanation, using the small γ-ray electroscope for measurements, and that when the emanation decayed to such an extent that the effect on this electroscope was too small, measurements could be continued on the large γ and finally on the β-ray electroscope.

Two thin-walled glass tubes, 60 cm. long and 1·5 cm.

[*] Soddy, Phil. Mag. [6] xxvii. p. 215 (1914).

internal diameter, were made, and into one was introduced, with the help of liquid air to get rid of uncondensed gases in the usual way, 14 millicuries of emanation, while in the other 0·07 millicurie was placed. It was estimated that the glass walls of the tube cut down the β rays to 31 per cent. of the total. The tubes were sealed at a capillary provided for that purpose, when only one bubble was obtained by each stroke of the Töpler pump; the sealed end will be referred to as the "liquid air end," while the round end will be spoken of as the "experimental end."

Method of Experiment.—Whenever the tubes were not in use, the liquid air end always stood in a depth of at least 5 cm. of liquid air, so that any time after three hours one could assume that there was no activity at the experimental end. When a determination was to be made, the tubes were withdrawn from the liquid air and the experimental ends quickly placed 5 cm. deep in a bath of pentane which had been previously cooled to some desired low temperature. After an exposure of 40 minutes, during which the temperature was kept constant, they were withdrawn and placed alternately under the electroscope for about 20 minutes, while measurements of activity were made, in a standard position in which all the tube, with the exception of 10 cm. of the experimental end, was screened by the heavy lead cylinder. The liquid-air ends were then replaced for at least three hours in liquid air before another experiment at a different temperature was made. Experiments for 40 minutes immersion of the experimental ends at liquid-air and room temperatures were also made. The weak tube was measured on the β-ray electroscope and the strong tube initially on the small γ-ray electroscope.

A series of such determinations for these two tubes at different temperatures were simultaneously made, and then the strong tube was laid aside for 10 days. Another set of experiments were made with it alone, measurements being made this time on the large γ-ray electroscope, after which it was laid aside for the same period, and then redetermined. This time the β-ray electroscope was used for measurements.

It was proved in the first place that all the emanation was condensed by liquid air by removing the liquid-air end from liquid air and immediately measuring the activity of the experimental end, when it was found that after extrapolation backwards, the activity at the instant of withdrawal was only 0·3 d.p.m., while after 40 minutes at the temperature of the room the activity was 18·8 d.p.m.

The activities obtained for a low temperature experiment

usually started three or four minutes after the removal of the tube from the pentane bath, and were extrapolated back to the instant of withdrawal. Some convenient instant was chosen, and by noting the interval of time between the time of experiment and the chosen instant, and by assuming the radium emanation to decay exponentially with a period of average life of 5·55 days, the quantity obtained above by extrapolation was multiplied by a factor to give the activity that would have been obtained had the experiment been carried out at the chosen instant. The effect of the decay of the emanation was thus eliminated. After this correction had been made the fraction of the emanation condensed is obtained by substituting in expression (1).

Results. — The curves obtained are shown in figure 4. Curve A is for the weak tube, curve B is the first curve for the strong tube, and curves C and D the second and third curves respectively for the same tube. Dealing first

Fig. 4.

Radium emanation in exhausted straight tubes.
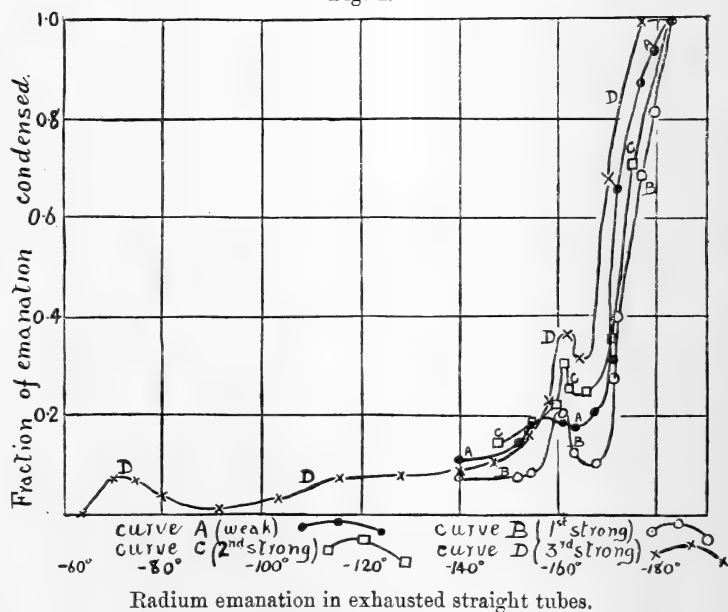
with the curves obtained from the strong tube, it is observed that each curve shows a marked maximum point at or near $-161°$ C., and that as the concentration becomes less the condensation curve is moved to the left. Thus curve D is roughly parallel to curve B, but about 8° C. to the left.

Curve C is intermediate in position. The curve for the weak tube approximates more closely to the first strong tube curve, and it is to be noted that although it exhibits no very marked maximum, there are three points that consistently indicate its presence. The last set of readings that was made with the strong tube was prolonged into comparatively high temperatures, and it is at once seen that there is a second maximum at about 72°·5 C., and that there is a long portion of the curve between 115° C. and 143° C. during which the fraction of the emanation condensed remains constant.

The results of this experiment show (1) that different tubes, in general, have different condensation curves, (2) that as the concentration of the emanation diminishes it becomes easier to condense, and (3) that there exist two maximum points, one at —161° C. and the other at —72°·5 C.

Luminosity Experiments.

The existence of at least one maximum point was then studied in another way. A good many years ago, Rutherford noticed that if a tube containing radium emanation was partially immersed in liquid air, the greatest intensity of the luminosity occurred just above the surface of the liquid air, and that as the level of the liquid air was raised the ring of greatest intensity was raised as well. This experiment was repeated by supporting a tube, containing 14 millicuries of emanation with a very small quantity of other gases, on a cork floating in liquid air. The ring of brightest intensity was obtained, but it was found that, no matter how long the tube was kept in liquid air, all the luminosity could not be obtained on this ring. There was still a large fraction scattered over that part of the tube beneath the level of the liquid air. It was proved that this ring was not due to a collection of ice nor due to a particular state of the glass, because the ring persisted after the whole tube had been warmed to room temperature. To test whether the effect was due to some electrical condition of the glass which would cause an accumulation of the active deposit in this particular region, even although there was no concentra-tion of the emanation, a glass tube, silvered on the inside, was filled with the above mentioned quantity of emanation. If the effect had been due to electrical causes, the silver would have dissipated any charge that had accumulated in one region.

The ring of intensified luminosity was still observed. The

only conclusion that can be deduced is that the vapour pressure of the emanation is lower at some temperature slightly higher than that of liquid air, than it is within certain limits of temperature intermediate between these two. That this low value of the vapour pressure is not lower than the value at liquid air temperature is shown by the fact that the emanation, no matter how long it is exposed to very low temperatures, will not collect completely in the region beyond the liquid air.

These observations, therefore, form further evidence of the existence of a maximum, probably the one at $-161°$ C., found in the quantitative measurements with the straight tube.

Experiments by another method in a two-limb tube.—Further experiments were made with radium emanation in a two-limb tube of the form shown in fig. 5. The greatest length of the

Fig. 5.
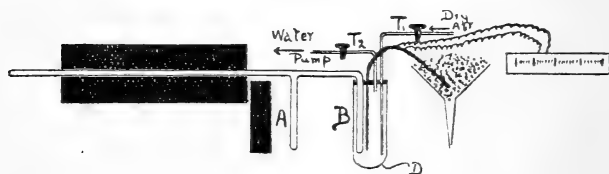
tube was 70 cm., while the short limbs were each 18 cm. long and were 15 cm. distant from one another. As before, 10 cm. of the long tube projected beyond the lead cylinder (the same as used previously) and the activity of the unscreened portion could be measured on either the small γ or on the β electroscopes, which occupied the same positions as previously described.

The end of limb A was always immersed in liquid air except when an experiment at some low temperature was in progress, while limb B was enclosed in the larger gas-tight tube D, through which a current of air, freed from CO_2 by soda-lime and from moisture by sulphuric acid, could be drawn by a water-pump. The taps T_1 and T_2 regulated the gas stream, and the end of the thermocouple was at the same level as the end of limb B.

The tube was charged with 14 millicuries of emanation. The advantage of this tube was that it was unnecessary to remove it from its position under the electroscope to make a determination.

The tube was kept at room temperature until the active deposit had come into equilibrium, and the γ activity of the exposed end was then determined as accurately as possible by repeated measurements. Limb A was suddenly plunged into liquid air, and γ-ray measurements were continuously made until the activity became very small, when alternate γ and β measurements were made for a time, after which the latter alone were continued. The β-ray measurements continued to decrease until the activity due to the tube was 6·9 d.p.m. Calculated from the factor obtained when alternate readings were made, it was found that the tube had an initial β-activity of 7550 d.p.m., so that taking the ratio of these two values, there is 0·0915 per cent. of the emanation uncondensed in a good vacuum at liquid-air temperature.

The determination of the condensation curve for the emanation in this tube was then proceeded with. The method was to regulate approximately the temperature registered on the voltmeter by surrounding the wide tube with a cylindrical flask of liquid air, a stream of air being kept continuously going through the tube. When the temperature was satisfactorily adjusted and the activity of the experimental end had been determined, the liquid-air vessel keeping the emanation condensed in limb A was quickly removed and continuous readings were made with the β electroscope for 10 to 15 minutes. The temperature was kept constant by altering the volume of air going through the wide tube. Limb A was replaced in liquid air exactly at the end of five minutes, and the increase of activity which had resulted during this time was read off from the curve and then a correction made, as previously explained, to eliminate the effect of the decay of emanation.

In these experiments, what was actually observed was the quantity of emanation volatilized, in distinction to the earlier ones which gave the amount of emanation condensed. The fraction of emanation volatilized is, therefore, B_T/B_R where B_T is the increase, after correcting for decay, obtained by exposing limb A to room temperature for the standard time when limb B is at the temperature T, and where B_R is the increase of activity similarly obtained when both limbs are exposed to room temperature. The fraction of emanation condensed f is therefore given by

$$f = 1 - \frac{B_T}{B_R}.$$

Results.—Fig. 6 shows the curves obtained ; all values were worked out by the same methods, but the points marked

Fig. 6.

Radium emanation in exhausted two-limb tube (fig. 5).
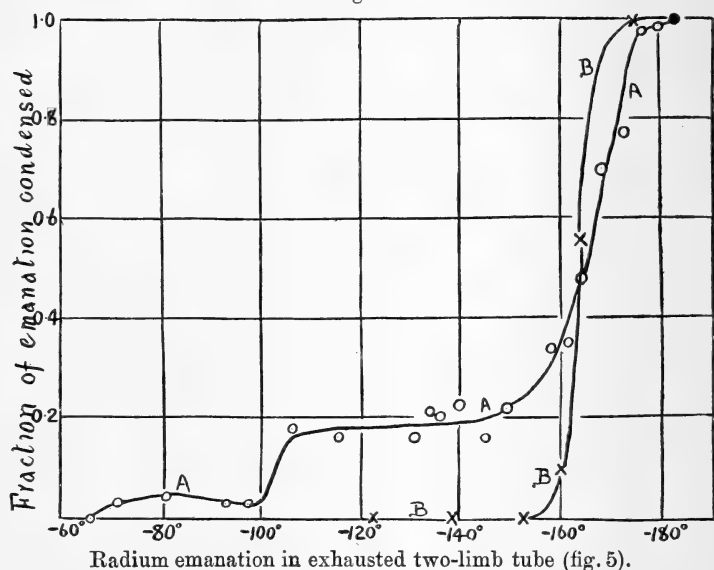
with circles were obtained between March 20th and 26th and those with crosses between the 26th and the 28th of the same month.   It will be seen that they lie on two curves, one of which crosses the other.

With reference to curve A, it will be noticed that here again there is evidence of a maximum point about $-80°$ C., but that there is no trace of the maximum previously obtained at $-161°$ C.   In view of the comparatively large variation of the points between $-100°$ C. and $-150°$ C., it is not wise to attach any value to the apparent change of slope at $-160°$ C.   It will be noticed also that the curve in the neighbourhood of the maximum is much less steep in this case than in the case of the maximum at $-72°$ C. in curve D (fig. 4).   This and also the absence of the maximum at $-161°$ C. may be due to the fact that in this experiment there is always a slow gradient of temperature owing to the upward current of air in the wide tube, whereas in the previous experiments, where pentane was used, the change from the low temperature to that of the room was very quick.

The second curve was obtained in the course of attempts to add more points and to verify those already obtained.

The surprising result was found that the points were lying on a totally new curve, that the emanation did not start to be condensed until after $-150°$ C., and that then it became completely condensed very quickly. At the conclusion of the experiment the vacuum of the tube had not appreciably deteriorated.

The only suggestion that can be made to explain the two curves is that some quantity of gas had been liberated from the walls of the tube which had a great effect on the condensation of the emanation. Whatever the cause, the results show the great difficulty attaching to experiments of this character.

Experiments at Low Pressure with Thorium Emanation.

Apparatus.—For the thorium experiments the same preparation of radio-thorium which had been used for the work at atmospheric pressure was put into a small cylindrical brass drum which was closed at the ends by filter-paper fixed on with sealing-wax. For the first experiments a straight tube was taken, fig. 7, at the bottom of which a small test-tube

Fig. 7.

P_2O_5 End — Glass-wool. Radio-thorium. — Experimental end.
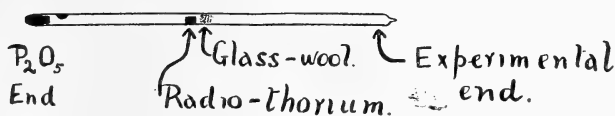
filled with phosphorus pentoxide was placed, and a depression was made in the glass so that this tube could not slide away from its end. The radio-thorium drum was then introduced and made to take up a position mid-way along the tube, where it was fixed by sealing-wax. There was also a glass-wool plug placed between the drum and the sealed end close to the former. The total length of the tube was 60 cm. and the diameter 1·5 cm.

The tube was thoroughly evacuated by attachment over night to a charcoal bulb cooled in liquid air, after which it was sealed. The two ends of the tube will be distinguished as the "P_2O_5 end" and the "experimental end." In this experiment the large γ electroscope, A, in the same position as shown in fig. 3, was used to measure the activities of the experimental end. For this purpose the tube was placed in the lead cylinder with 10 cm. of that end projecting to the right.

The P_2O_5 end was placed in liquid air and allowed to stand

there for three days, and then the activity of the experimental end was determined.   This quantity was found to be be 2·90 d.p.m., and it must be treated as an additional "natural leak" and always deducted from any subsequent measurements.

Test for instantaneous diffusion.—An experiment to determine whether the assumption as to instantaneous diffusion was justified was carried out with this tube.

The P_2O_5 end was allowed to stand in liquid air for three days, and then the activity (I_F) of 10 cm. of the P_2O_5 end was measured.   This gave the activity due to the equilibrium amount of active deposit that could be collected at this end. The experimental end was then immersed for the same time in liquid air and the activity (I_N) of the equilibrium amount of active deposit that could be collected at this end found. The values of these quantities were respectively 332·6 d.p.m. and 319·1 d.p.m.

Let k be the fraction of the emanation present in one half of the tube crossing the glass-wool plug per second, to the other half;

Q, the total amount of emanation set free from the drum :

n the number of molecules that cross the glass-wool plug per second from the P_2O_5 end to the experimental end;

and m the number that cross in the reverse direction.

For the P_2O_5 end in liquid air, $I_F = Q$, and for the experimental end in liquid air $\lambda I_N = n - m$; but in this case $m = 0$, and therefore $\lambda I_N = n$:

but
$$n = k(Q - I_N) = \lambda I_N,$$
$$\therefore \qquad I_N(k + \lambda) = k I_F,$$
$$\therefore \qquad I_N/I_F = k/(k + \lambda).$$

Since I_F is nearly equal to I_N, it follows that k must be very large compared with λ ; *i. e.* that the fraction of emanation diffusing through the glass-wool plug is very large compared with the fraction decaying per unit time.   The assumption as to instantaneous diffusion in the case of this thorium emanation tube is therefore justified, and it follows that in the case of radium emanation, where there is no glass-wool plug, instantaneous diffusion also takes place.

Method of Experiment.—The method of making a determination of the fraction of emanation condensed at any particular temperature was as follows.   The P_2O_5 end had

been standing for at least four hours in liquid air, so that it could be assumed that any activity more than the irreducible quantity mentioned above was decaying exponentially with the period of thorium B. The tube was withdrawn from liquid air, and during the ensuing 40 minutes the activity, L, in excess of the irreducible activity at the beginning of that interval was determined. At the end of that period of time the experimental end was placed 5 cm. deep in a pentane bath previously cooled to some low temperature. After a 40 minutes' exposure at this temperature, the experimental end was withdrawn and the P_2O_5 end replaced in liquid air for another definite time, $3\frac{1}{2}$ hours, when the tube was again withdrawn from liquid air and the activity, N, of the experimental end determined as quickly as possible. Then the P_2O_5 end was again placed in liquid air for at least four hours before another determination at some other temperature was made.

When the measurement N is being made, the quantity L will have decayed to $L \times e^{-\lambda t}$, where λ is the radioactive constant of thorium B and t is the time that has elapsed between making the measurements L and N. In determining the initial leak prior to the exposure, the emanation is uniformly distributed throughout the tube and a certain quantity of active deposit will be obtained on the experimental end. The activity from this active deposit is exceedingly small while that measurement is being made but will not be, by any means, negligible when the final measurement is taken. If, however, the time during which the initial measurement is made is always constant, the final measurement will be the sum of three quantities, the quantity $Le^{-\lambda t}$, a variable quantity due to the 40 minutes' exposure at some low temperature, and a constant quantity due to the uniform distribution of the emanation during the initial measurement. The activity, D, due to the 40 minutes' exposure is therefore given by

$$D = N - Le^{-\lambda t} - Q, \quad \cdots \quad (2)$$

where Q is a constant activity due to active deposit collected during the uniform distribution while the initial measurement is being made. The fraction of emanation condensed at any temperature T is obtained by finding the values of D for that temperature, room and liquid air temperatures, and substituting the values D_T, D_L, and D_R for A_T, A_L, and A_R in expression (1). The numerator and the denominator of this expression therefore consist of the difference of two values for the expression (2), and therefore the quantity Q does not

require to be known.   It is only necessary to keep the time employed in making the initial measurements always constant.

Results.—The curve obtained is shown in curve A, fig. 8. It exhibits no points that require detailed reference, but it will be observed that the shape of the curve is similar to that obtained by Rutherford and Soddy for thorium emanation mixed with air at atmospheric pressure.   The greater part of the emanation is condensed between $-165°$ C. and $-170°$ C.

Fig. 8.
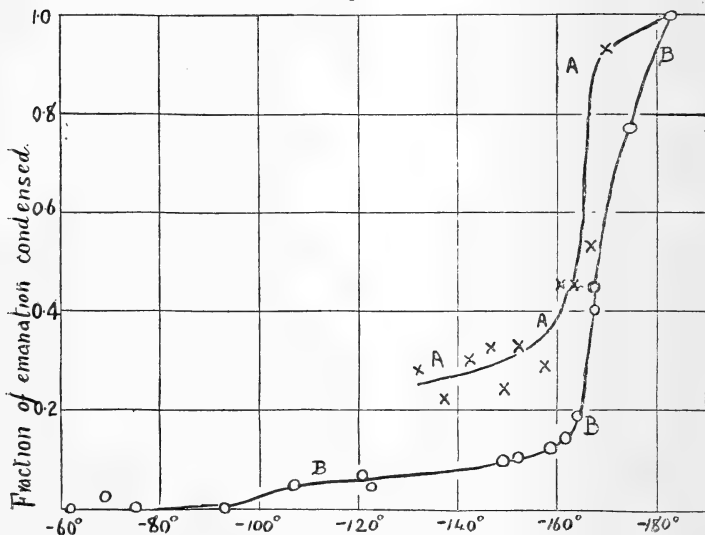
Curve A. Thorium emanation in exhausted straight tube (fig. 7).
Curve B. Thorium emanation in exhausted bent tube (fig. 9).

As the net activity for the amount of emanation condensed at liquid air temperature was only 11 d.p.m., the curve was not prolonged to high temperatures.

Experiments at Low Pressure with Mixed Thorium and Radium Emanations.

Apparatus and Method of Experiment.—Experiments were now started on the mixed emanations in a sealed tube at low pressure.   A new type of tube, as shown in fig. 9, was constructed of glass permeable to β rays and was filled with 0·07 millicurie of emanation.   The thorium preparation was slightly stronger than that used in the previous experiment, and was, as before, in a filter-paper drum which was fixed

in the bulb of the tube by sealing-wax. β rays only were used and the electroscope was in the position relative to the lead cylinder shown in fig. 3.

The short limb of the tube is the P_2O_5 end, and 10 cm. of the long limb is the experimental end.

Fig. 9.

The advantage of this tube is that the activity can be determined prior to the exposure without removing the P_2O_5 end from liquid air.

The P_2O_5 end was, as before, immersed for three days in liquid air, and the irreducible activity of the experimental end determined, and this quantity is always treated as a natural leak. As in the thorium straight tube, the P_2O_5 end must always have been four hours at least in liquid air before a determination at some temperature is carried out.

The following is the method of carrying out such a determination. The activity, L, of the experimental end was measured. The tube was then removed from the lead cylinder and the experimental end placed as quickly as possible 5 cm. deep in a pentane bath previously cooled to some low temperature T. After 40 minutes of exposure at this constant temperature, the tube was replaced in the lead cylinder and the P_2O_5 end immediately immersed in liquid air. The activity of the experimental end is determined during the 15 minutes following this replacement, and then the final measurement is made after the P_2O_5 has been immersed in liquid air for $3\frac{1}{2}$ hours.

The curve obtained from the measurements made during the time immediately following the exposure is extrapolated back to the instant of withdrawal of the tube from the pentane bath. Let the quantity so obtained be M, and let the final activity be N. M is made up of three factors, (a) the activity contributed by L, *i. e.* $L \times e^{-0.7\lambda}$, since t for the time of exposure = 40 minutes ; (b) the activity contributed by thorium active deposit obtained during the 40 minutes' exposure ; and (c) the active deposit from the radium emanation condensed during that exposure. (c) when found can be taken as a measure of the radium emanation condensed. It is better, however, for the sake of accuracy to allow (b) to increase to its maximum and to measure it after $3\frac{1}{2}$ hours. If E is the maximum activity obtained from the thorium

emanation condensed, then $E = N - Le^{-5\lambda}$, since $t = 5$ hours. When the experiment has been carried out for room and liquid-air temperatures, the fraction of the emanation condensed is found by substituting the values of E_T, E_L, and E_R in the expression (1). The value of (c) cannot yet be determined.

A whole series of such determinations were made, and then the tube was laid aside until no trace of the radium emanation could be detected. A large number of determinations as described above were then made for liquid-air temperature alone, and the average value of the ratio

$$\frac{M - Le^{-0\cdot7\lambda}}{N - Le^{-5\lambda}}$$

was found. This was determined as $0\cdot326$.

This factor was then used to multiply all values of $\{N - Le^{-5\lambda}\}$ obtained during the experiments with the mixed emanations, and for each temperature in that set of experiments the value of

$$0\cdot326\{N - Le^{-5\lambda}\} + Le^{-0\cdot7\lambda}$$

was subtracted from the corresponding value of M. The result gives a measure of the radium emanation condensed at a particular temperature at a certain time. The value so obtained was corrected for the progressive decay of the radium emanation as before to the value, G, which would have been obtained had the experiment been carried out at the chosen instant. The value of G is determined for room and liquid-air temperatures and, as before, the fraction condensed is obtained by substituting G_T, G_L, and G_R in the expression (1).

Example.—An example, for which the detailed curves obtained are shown in fig. 10, will make the calculation clearer. Curve A shows the curve obtained from the measurements taken over the whole six hours during which the experiment was carried out, while curve B is obtained by plotting on a larger scale the measurements made immediately after the exposure at the low temperature. This latter curve was used to obtain the value of M.

Temperature of experiment,		$-159^\circ\cdot5$ C.
Time of experiment,	1 day after chosen instant.	
Initial activity	=	$26\cdot0$ d.p.m.
Irreducible activity	=	$4\cdot8$ d.p.m.
∴ Value of L	=	$21\cdot2$ d.p.m.
Activity after exposure	=	$80\cdot5$ d.p.m.
∴ Value of M	=	$75\cdot7$ d.p.m.

Activity after $3\frac{1}{2}$ hours	=	44·8 d.p.m.
$\therefore$ Value of N	=	40·0 d.p.m.
$L \times e^{-0\cdot7\lambda}$	=	20·35 d.p.m
$L \times e^{-5\lambda}$	=	15·30 d.p.m.
$\therefore E_T = N - Le^{-5\lambda}$	=	24·70 d.p.m.

and $M - 0\cdot326(N - Le^{-5\lambda}) - Le^{-0\cdot7\lambda}$

$= 75\cdot7 - 8\cdot05 - 20\cdot35 = \quad 47\cdot30$ d.p.m.

Fig. 10.
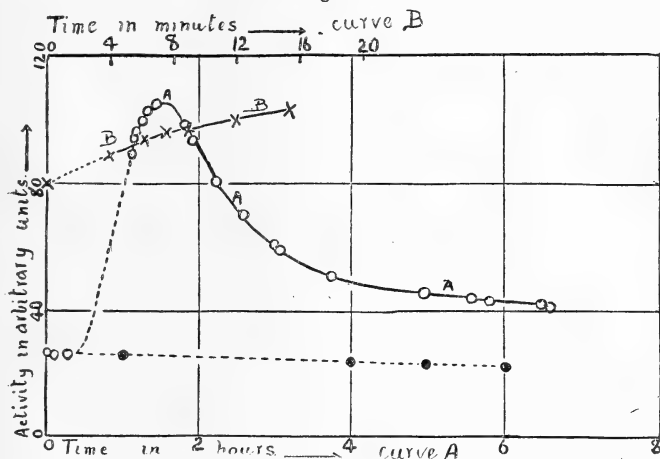
Example of observations used to plot curves shown in Fig. 12.

Since the experiment was performed one day after the chosen time this last quantity has to be multiplied by 1·2 to eliminate the effect of decay. This gives the value of G_T to be 56·6. It was found in other determinations that E_R and E_L were respectively 6·3 and 57·5 and that G_R and G_L were 10·9 and 101·8. The fraction of thorium emanation condensed at $-159^\circ\cdot5$ C. is therefore

$$\frac{24\cdot7 - 6\cdot3}{57\cdot5 - 6\cdot3} = 0\cdot359 ;$$

and of radium emanation at the same temperature,

$$\frac{56\cdot6 - 10\cdot9}{101\cdot8 - 10\cdot9} = 0\cdot503.$$

Variation of the fraction of the emanations condensed at liquid-air temperature with lapse of time.—Another complication arose, however, in this experiment from a cause

2 A 2

similar to that already discussed (page 348) and shown in fig. 6, namely, the alteration in the behaviour of the tube in successive measurements. During the course of the experiments three exposures of the tube were made at liquid-air temperature, and it was noticed that the quantities of emanation obtained in the experimental end (after all corrections had been made) became smaller as time progressed. When these quantities were plotted against the time, it was found that in both cases the points lay on a straight line as shown in fig. 11. It is further observed that the same percentage decrease is obtained in both cases. This is an important observation, and if it could be confirmed, it would be strong indirect evidence that these emanations are non-separable by condensation. This introduces an uncertainty but, from the fact that the points in fig. 11 lie on straight lines, it was considered justifiable to correct for this by reading off the values for E_L and G_L at intermediate times from the curve (fig. 11).

Fig. 11.

Points for Radium are marked O. Thorium points are shown X.
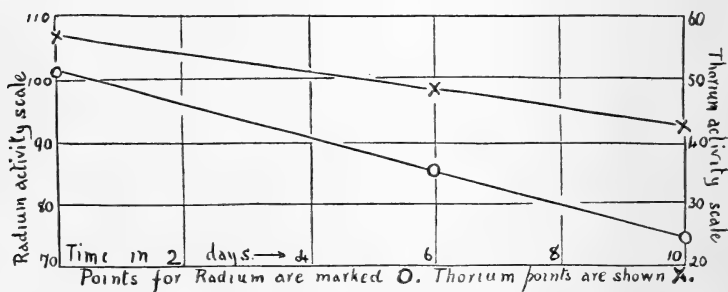
Curves showing progressive change of the proportions of emanations condensed at liquid-air temperature in the same tube with lapse of time.

Results.—The different fractions obtained at various temperatures are shown in the accompanying table, and also numbers to indicate the order in which the experiments were made. It is at once seen that at any temperature the fraction of radium emanation condensed is greater than the corresponding fraction for thorium emanation. Viewed as a whole, this is the only result that can be arrived at, that radium emanation appears more easily condensed than thorium emanation. When more fully examined, however, the points separate themselves into two lots each of which lies on a curve. These curves have been separated and are

TABLE.

		THORIUM EMANATION.			RADIUM EMANATION.			
Temperature.	Order in which exper. was made.	Numerator of expression(1).	Denominator of expression (1). Read from fig. 11.	Fraction condensed.	Numerator of expression(1).	Denominator of expression (1) from fig. 11.	Fraction condensed.	Set of curves to which points belong.
−138°	7	0·1	46·8	0·0024	10·1	83·4	0·121	A
−147°·2	3	2·3	54·0	0·0426	9·1	96·0	0·095	A
−152°·6	9	1·8	45·05	0·0399	11·9	79·6	0·149	B
−155°·2	2	2·3	54·25	0·042	18·55	96·5	0·192	B
−159°·5	5	16·5	51·2	0·359	45·70	90·9	0·503	B
−161°·5	11	1·9	43·6	0·0435	7·6	76·8	0·099	A
−164°	4	28·5	52·6	0·541	70·85	93·0	0·762	B
−164°	13	7·7	42·0	0·183	31·8	74·0	0·43	A
−166°	8	21·3	46·3	0·46	54·1	81·9	0·667	A
−167°·5	1	38·7	55·9	0·693	97·6	99·2	1·0	B
−167°·5	14	15·7	40·0	0·343	47·5	70·1	0·677	A
−170°	10	20·7	44·9	0·462	55·7	79·0	0·705	A
−173°	6	39·7	51·0	0·779	94·3	90·0	1·0	B
−180°	12	36·2	43·2	0·839	64·6	76·1	0·849	A

shown in fig. 12, and are to a certain extent similar to the
pair of curves shown in fig. 6.   There is, however, this
difference, that consecutive points in the former experiment

Fig. 12.

Points for radium are shown thus   ●—●—●
.   .   thorium   ,,   ,,   ,,   ×—×—×
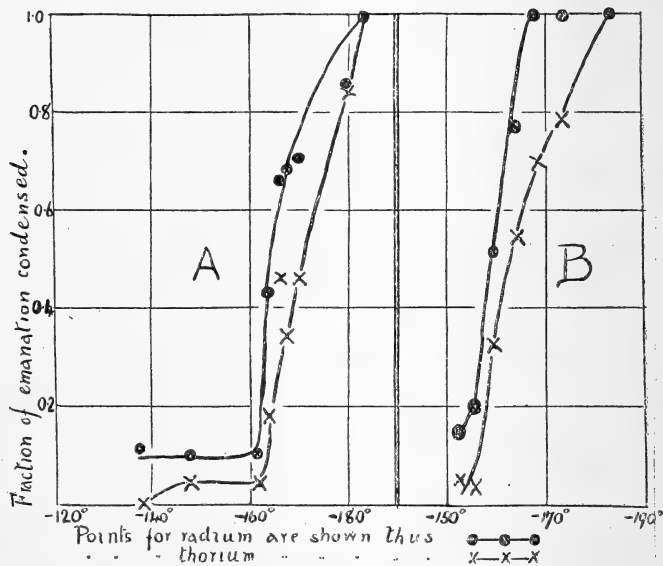
Curves obtained for mixed radium and thorium emanations in
exhausted tube (fig. 9).

lie on the same curve, but in this latter consecutive points
may lie on either.   The curves of set A are roughly parallel
to but from 7 to 10 degrees lower than those of set B.

Repetition of this experiment.

A second experiment which was made was mainly concerned
with an endeavour to repeat the previous observations with
regard to the proportional decrease in the quantity of emanation
condensed as time went on.   The β-ray electroscope remained
in its former position, but the small γ-ray one was placed
close to the P_2O_5 end, so that the total amount of emanation
condensed in this end could also be determined.

Another quantity of radium emanation was sealed in the
tube, and the determination of the quantity of emanation
condensed by liquid air was made every third day.   Only
one experiment was made for a higher temperature, and it
confirmed the previous result that radium emanation was
apparently more easily condensed than the thorium emanation.

However, it was found in this case that the quantities of thorium and radium emanations condensed on different dates remained appreciably constant, and that therefore the proportional diminution effect was not an invariable property of the mixed emanations.

Thorium Emanation alone.

An opportunity was taken after all the radium emanation had decayed to determine the condensation curve for thorium emanation alone in this tube.

The experiments were carried out as explained on page 353, and the values for E and the fraction of emanation condensed as stated on page 354.

The curve obtained is shown in fig. 8, curve B, and it is seen that the greater part of the emanation is condensed from $-162°$ C. to $-180°$ C.

Theory of the Experiment.

It is difficult to compare the preceding experiments, where the fraction of the emanation condensed at a given temperature has been studied, with the condensation of an ordinary gas where the vapour-pressure of the gas rather than the fraction condensing is a function of the temperature. It may, however, be pointed out that even were the radium and thorium emanations physically identical as regards volatility, a difference in the direction found, namely, that the shorter lived emanation will appear more volatile, is to be expected under certain circumstances. In the case of thorium emanation there is a steady supply of, say, x atoms per second to the gaseous phase and a steady disappearance of the same number per second, Ax from the condensed phase, and $(1-A)x$ from the gaseous phase, where A is the fraction condensed. Equilibrium is established when Ax more atoms enter the condensed phase per second than leave it. In the case of radium emanation, the numbers entering and leaving the condensed phase are equal. In the case of mixed emanations, indistinguishable in volatility, the ratio of the concentration of thorium to radium emanation must be higher in the gaseous than in the condensed phase, since the ratio of thorium to radium emanation condensing is higher than the ratio of thorium to radium emanation volatilizing. Hence the thorium emanation must appear more volatile. Whether or not this effect is large will involve the absolute time which, on the average, a molecule of emanation spends in the gaseous phase before entering the condensed phase. If this is comparable with the period of average life of the atom, the effect will be marked.

Let the fraction of the condensed emanation entering the gaseous phase per second be q, and of gaseous emanation entering the condensed phase per second be p, so that $1/q$ and $1/p$ represent the average lives of the emanation molecule in the condensed and gaseous phases respectively. Let the fraction of the total emanation condensed be A.

For the radium emanation

$$q A_R = p(1 - A_R)$$

or
$$p/q = \frac{A_R}{(1 - A_R)}$$

For the thorium emanation

$$q A_T + \lambda A_T = p(1 - A_T)$$

or
$$\frac{p}{\lambda + q} = \frac{A_T}{1 - A_T}.$$

Consider now a case where the radium emanation would be completely condensed and where the thorium emanation once condensed does not volatilize again, *i. e.* let $q = 0$. The thorium emanation is not completely condensed unless λ is negligibly small compared with p. The ratio of the condensed to uncondensed portion is that of p to λ, or of $1/\lambda$ to $1/p$, that is the ratio of the period of average life of the thorium emanaion to its period of average life in the gaseous phase before condensing. If $1/\lambda = 1/p$, that is, if, on an average, the emanation spends 78 seconds after formation before condensing, only one half will be condensed. The results obtained may therefore be due to the rapid disintegration of the emanation and the apparent separation effected by condensation may be a time separation of isotopes differing in period, which is familiar enough, rather than due to a true difference of volatility.

General Remarks.

It is observed in these experiments that the radium emanation condensation curves have only the slightest resemblance to each other, and the same remark applies to the thorium emanation curves. Any quantity of emanation in an exhausted sealed tube has at least one, and may have two, condensation curves peculiar to itself. The natural conclusion to be derived is that the residual gases play an important part in determining the condensation curve of emanation in any particular tube. This is perhaps not to be

wondered at, as their concentration may be many times as large as the concentration of the emanation.

In none of the experiments with thorium emanation nor with mixed emanations has any trace of the maxima previously observed been found, and their presence in the earlier experiments, therefore, seems to be due to special circumstances. The fact that they were not found when P_2O_5 was enclosed in the tube, suggests that the presence or absence of water vapour may have a deciding influence. They might, of course, be due to the formation of a molecular complex, but at present there is no evidence on which a decision as to their cause can be based.

It is worth noting that these experiments involve, for the first time, the consideration of the time which an atom spends in the gaseous phase in equilibribrium with a liquid. In the case of thorium emanation, a determination of this magnitude might be based on methods similar to those here employed, if the true condensation curve could be determined.

Summary.

(1) When thorium and radium emanations are mixed with air at atmospheric pressure, thorium emanation appears to be condensed about 5° C. above the radium emanation.

(2) This apparent difference is probably due to the radium emanation in the gaseous phase over the condensed phase being swept away by the air current.

(3) As the concentration of the emanation in a highly exhausted tube diminishes the emanation becomes more easily condensed.

(4) In certain circumstances the condensation curve of radium emanation exhibits two maxima, one about −75° C. and the other about −161° C. It is suggested that the existence of this property may be dependent on the presence of water vapour.

(5) The existence of at least one maximum in the condensation curve is confirmed by studying a glass tube, containing a large quantity of radium emanation, floating vertically in liquid air. A ring of bright luminosity occurs just above the surface of the liquid air, and this ring is not due to a condition of the glass nor to a concentration of the active deposit away from the emanation.

(6) Internal changes are liable to take place inside the tube which will completely alter the condensation curve obtained.

(7) At liquid-air temperature in a highly exhausted tube

0·0915 per cent. of radium emanation remained uncondensed in the one determination that was made.

(8) The condensation of thorium emanation in a highly exhausted tube was also studied.

(9) When the two emanations are mixed in such a tube the radium emanation appears to be more easily condensed.

(10) This may not be due to a real difference in the condensation points but is probably caused by the rapid disintegration of the thorium emanation.

(11) In one experiment indirect evidence was obtained which seems to point to thorium and radium emanations being non-separable by condensation.

I desire to take this opportunity of expressing my thanks to Professor F. Soddy, F.R.S., for the strong thorium preparations and quantities of radium emanation, for the preparation of the tubes employed, and for the section entitled "Theory of the Experiment" in this paper for which he is responsible. I am indebted to him also for his interest in the experiments throughout their entire course.

I have to thank Miss Hitchins, B.Sc., also for the capable assistance which she gave me in carrying out the manipulations and lengthy measurements involved.

Physical Chemistry Department,
    Glasgow University.
December, 1914.

XXXIX. *On a Qualitative Method of Investigating Thermionic Emission.* By F. Lloyd Hopwood, *B.Sc., A.R.C.Sc.*[*]

THE present writer discovered some time ago [†], that the movement of charged bodies in the neighbourhood of a glowing carbon-filament lamp produced, under certain circumstances, a displacement of the loops of the filament.

Similar observations were recorded by Eve [‡] at about the same time. The results of a further study of the phenomena and their application as a basis of a qualitative method of investigating the emission of electrified particles from incandescent bodies, are set forth in the present paper.

Experiments with Carbon Filaments.

When an electrified rod, charged with electricity of either sign, is brought near an *unlighted* ordinary 200-volt carbon-filament lamp, the loops diverge in a similar manner to the

leaves of an electroscope, the divergence disappearing on the removal of the charged rod.

If a *negatively* charged rod is brought near the lamp when the filament is glowing, the loops diverge, the divergence again disappearing on the removal of the rod, or if the filament touches the glass walls of the lamp.

When, however, a *positively* charged rod is brought towards the glowing filament, no movement of the loops occurs. On rapidly removing the positively charged rod from the neighbourhood of the glowing filament the loops diverge. If the divergence is sufficiently great for the loops to touch the glass walls of the lamp, they immediately spring back to their original position, but if they do not touch the walls, they will remain in the displaced position, in some cases for several minutes. When in the displaced position produced in this way, the loops respond very readily to the movement of any bodies whether charged or uncharged, in their neighbourhood—" twiddling " the fingers near the lamp sets them into violent vibration. Placing the bulb momentarily in contact with the metal cap of an electroscope gives a negative charge to the leaves.

Should the bulb be touched by the hand or a Bunsen flame be rapidly passed over it, the displacement of the loops, their response to the movement of an uncharged body, and the ability of the bulb to charge an electroscope on contact, all disappear.

The above effects may be explained as follows :—

It is well known that when a carbon filament is raised to incandescence in the neighbourhood of a cold conductor maintained at a positive potential, both being enclosed in an evacuated vessel, a continuous stream of electrons passes from the hot filament to the cold conductor. The emission under these circumstances has been studied in great detail by Richardson [*] and others. If the cold conductor is not maintained at a positive potential by external means, the emission from the hot filament proceeds until a certain limiting difference of potential between the filament and cold conductor is attained. This limiting potential depends on the geometrical configurations of the cold conductor and the hot filament, and its value has been obtained in certain cases, both theoretically and practically, by W. Schottky [†]. In the case of an ordinary carbon-filament lamp, this limiting potential difference is quickly established between filament and walls of bulb when the filament is glowing, and an

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[*] Richardson, Phil. Trans. 1903.
[†] *Deutsch. Phys. Gessell., Verh.* xvi. 10, May 1914.

equilibrium state is attained.   On bringing up a *negatively* charged rod, no further electronic emission can take place and the loops diverge in a similar manner and for the same cause as the leaves of an electroscope.   When a *positively* charged rod is brought up, the conditions are made more favourable to the electron emission, and the negative charge induced on the filament by the rod escapes from the filament to the walls of the lamp, giving a negative charge to the inner surface of the bulb on the side nearest the rod.   Thus, owing to the escape of the induced charge, the loops are unaffected by the *approach* of a positively electrified rod. Before the removal of the rod, the filament will be in equilibrium under the joint action of the charges on the rod and on the inner surface of the bulb.   On the *removal* of the positively charged rod, the negative charge on the walls induces a positive charge on the filament and produces the observed displacement of the loops.

Touching the bulb with the hand or playing a Bunsen flame on it, neutralizes the negative charge on the inner surface by permitting the accumulation of a positive charge on the outer surface of the bulb.   The charging of the electroscope is obviously due to the same cause.

The response to the motion of the hand will be due partly to a redistribution of the charge on the walls and partly to a change in the potential difference between filament and walls.

Null Effect at High Temperatures [*].

When various carbon filaments were heated above their ordinary temperatures by running the lamps above their normal voltage, they were found to be insensitive to the motion of charged bodies in their neighbourhood, although they were very sensitive to such motions at lower temperatures.

It was sometimes found that filaments of high candle-power lamps were also insensitive when run at their normal voltage, but sensitive at lower voltages (temperatures).

It was thought that the null effect in these cases might be due to one of the following causes :—

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[*] In a preliminary note on this effect which appeared in ' The Electrician ' of July 31, 1914, a different explanation from that given in the present paper was advanced, but in the light of further experiments has had to be abandoned.

a. An anomalous increase in the flexural rigidity of the filament owing to some change in structure due to a molecular rearrangement such as is known to occur in iron and silica at high temperatures ;

b. The residual gas in the lamps becoming ionized to such an extent by the hot filaments that it acts as a protective conducting-sheath towards external electrostatic fields ;

c. The emission of both positive and negative ions in sufficient quantities to neutralize an induced charge of either sign on the filament.

Experiments were carried out to test these hypotheses.

Some difficulty was experienced in devising an experiment to test the mechanical properties of a carbon filament at high temperatures, but finally the lamp shown in fig. 1 was used for this purpose. The filament was subjected to stress by

Fig. 1.

Fig. 2.
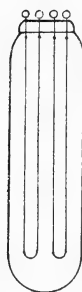
placing it in a fairly strong magnetic field while the heating current passed through it.

No evidence of any increase of rigidity with rise of temperature was obtained, the yield of the filament increasing with rise of temperature for all the temperatures used.

To test hypotheses (*b*) and (*c*), an incandescent lamp with two similar unanchored "hairpin" filaments was used (see fig. 2). On subjecting the residual gas to the ionizing action

of the beta rays from 20 milligrammes of pure radium bromide, and to both hard and soft X-rays from a powerful X-ray tube, it was found that, when due precautions were taken to prevent the discharge of the charged rods by the atmospheric ionization produced by the radiations, any ionization of the residual gas *in* the lamp had no appreciable influence on the displacement of the filament.

Galvanometric measurements of the thermionic current between one filament when raised to incandescence and the other (cold) filament, when the cold filament was maintained first at a positive potential and then at a negative potential, showed a comparatively large negative emission, but gave no certain indication of a positive emission from the hot filament. Air was then readmitted into the lamp and pumped out again by means of a Töpler pump. It was noticed that when the filaments were first raised to a dull red heat after the re-evacuation of the lamp, a *positively* charged rod produced a divergence on *approach* and a negatively charged rod a displacement of the loops on removal, thus showing that at the low temperature at which this took place, the filament emitted positive ions only.

This effect was only temporary and disappeared on continued heating.

The experiments of Richardson, Wilson, and others[*] show, however, that in similar cases a small permanent leak of positive ions still persists after the larger temporary one has disappeared, and that this leak (which can only be measured by an electrometer method) is very much greater at high than at low temperatures, although at the higher temperatures it is much smaller than the negative emission.

Now in the present experiments the inducing charges, though at high potential, are very small[†], so we may conclude for the reasons given above that the null effect at high temperatures is due to the emission of sufficient positive and negative ions to remove the induced charges, while the positive emission at lower temperatures is too small to dissipate the charges induced by the negative rod sufficiently quickly to prevent the motion of the filaments.

Experiments made with glowing platinum filaments in the open air tend to confirm this conclusion, for at a red heat

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[*] *Vide* J. J. Thomson, 'Conduction of Electricity through Gases,' 2nd. ed. p. 214; and Schottky, *Phys. Zeitschr.* July 1914.

[†] Glass rods rubbed with silk, and ebonite rods rubbed with flannel, were used throughout.

they were found to be attracted by a positively electrified but not by a negatively electrified rod, while at temperatures near the melting-point of platinum neither rod attracts the filament. It is of course well known that platinum in air emits chiefly positive ions at low temperatures and an excess of negative ions at high temperatures.

Experiments with Metal Filaments.

The knowledge that a glowing filament is attracted by a rod charged with electricity of the same sign as the ions emitted by the filament, and that the *removal* of a rod charged with electricity of opposite sign causes a movement of the filament provided there is a solid dielectric between them on which to receive the ions, has been used by the author as the basis of a qualitative method of investigating thermionic emission.

As the results obtained from experiments on the alloy nichrome are typical of those obtained from the metals and alloys mentioned below, a detailed account for this case only will be given.

A long filament (40 to 50 cm.) of No. 40 S.W.G. nichrome wire was attached by silver solder to the leading-in wires of a metal-filament lamp from which the glass envelope and original filament had been removed (see fig. 3).

This method of suspension was found to be most convenient and possesses the advantage that it is readily connected to the ordinary lighting circuit by means of the usual bayonet-type holders.

Fig. 3.

At a dull red-heat the filament was readily attracted by a rod charged with electricity of either sign, showing that there was no appreciable thermionic emission of either sign at this temperature.

At a bright red-heat (current 1·5 amps.) the filament was attracted by a positively charged rod, but not by a negatively charged one. A sheet of glass was then interposed between the filament and the charged rods. This had no influence on the action of the positively electrified rod, but the filament was attracted towards the glass screen when a negative rod was removed from its neighbourhood.

For the purpose of investigating the emission in air at pressures less than the atmospheric pressure, and in other

gases, the filament was mounted in the apparatus shown in fig. 4. The use of the ground-glass stopper facilitated the replacement of one filament by another, while the side tubes permitted the introduction of different gases and the regulation of the pressure by attachment to a pump. The hot nichrome showed the attraction produced by a positively charged rod and the kick due to the removal of a negatively charged rod in air at atmospheric pressure and at pressures down to less than one centimetre of mercury.

Fig. 4.

It gave similar indications in hydrogen and CO_2.

We conclude that nichrome at a bright red-heat in air, hydrogen, and CO_2 emits a large number of positive ions, and that its negative emission is insignificant.

Of the following metals and alloys all were tested in air and a few in hydrogen and CO_2. In every case they gave a positive emission.

The substances examined were :—

Iron, nickel, copper, nichrome (an alloy of nickel and chromium), brass, phosphor-bronze, silicon-bronze, platinoid, eureka, tinned copper, and " galvanized " iron.

So far as the writer is aware, the emissions from most of the alloys mentioned above have not previously been investigated.
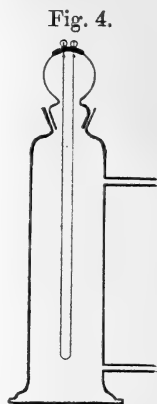
Advantages of the Method.

The method of investigation outlined above is very suitable for a rapid qualitative examination of the emissions from a large number of substances in air, and other gases, at various pressures. It requires no special manipulative skill, and use is made of only such apparatus as is generally found in a Physics Laboratory. It provides some striking lecture experiments. Incidentally, it was noticed that incandescent filaments mounted as above (fig. 3) are very susceptible to the approach of a magnet, and the laws governing the mechanical action of a magnet on current-bearing conductors may be readily demonstrated to large audiences by their use.

Summary.

Experiments are described illustrating the difference in behaviour of incandescent carbon filaments under the influence of small positive and negative charges. Explanations are

given of the observed effects and also of the null effect obtained at very high temperatures. A method of investigating qualitatively the thermionic emission from various bodies is developed and applied to the case of the emissions from wires of various alloys in air and other gases. A number of these had not previously been investigated.

In conclusion the author desires to express his indebtedness to Professor A. W. Porter, F.R.S., and to Professor O. W. Richardson, F.R.S., for their interest in the above experiments, and to thank the Staff of the Electrical Department of St. Bartholomew's Hospital for placing their powerful X-ray installation at his disposal, and for the use of their standardized amount of radium bromide.

XL. *The Ionization of Metals by Cathode Rays.*
By NORMAN CAMPBELL, *Sc.D.**

1. IN the Philosophical Magazine for August 1914 (p. 286), some experiments on the ionization of platinum by cathode rays were described. It appeared that considerable changes in the amount of ionization produced might be effected by heating the metal or making it the cathode of a discharge through oxygen. In order to throw light on the precise nature of these changes it appeared desirable to extend the observations to other metals and to cathode rays of higher speed. Such an extension is made in the observations now to be described.

2. A slight alteration was made in the essential part of the apparatus shown in fig. 1 of the last paper. Fig. 1 of this paper shows the new arrangement. A and B are nickel-plated brass cylinders. In A the cathode rays are produced from the Wehnelt cathode W and caused to enter B with a speed V_1 by keeping A at a potential V_1 higher than W. The rays fall on the plate P, the ionization of which is under investigation ; the speed, V, with which they strike P is varied by varying the potential V_2 between A and P. The electrons leaving P fall on B ; the potential between B and P will be called U, and will be counted positive when P is positive.

Two quantities have to be measured : i, the total current carried by the rays falling on P, and i_2, the current received by P when none of the rays reflected from P or the electrons emitted from P by its ionization fall back on P. R, the reflexion coefficient, in terms of which all the results are

conveniently expressed, is $(i_1 - i_2)/i_1$. If there is only reflexion and no ionization or only ionization and no reflexion, then R is a measure of the reflexion or the ionization respectively.

Fig. 1.
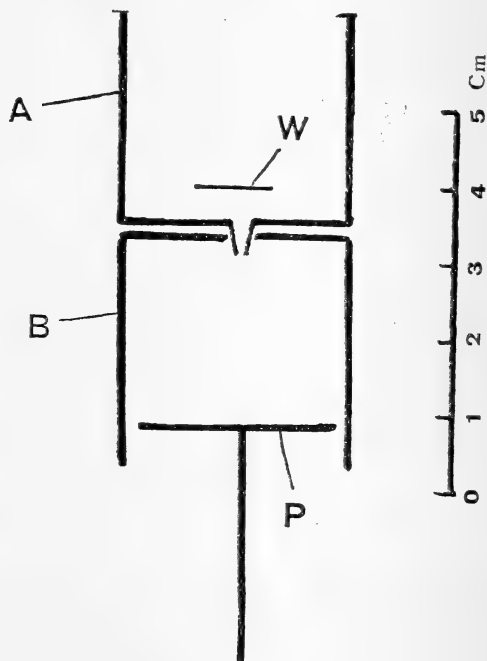
i_2 can easily be measured by making U negative ; it was found that i_2 was saturated when $U = -20$ volts ; this value was sufficient to prevent any of the rays leaving P from striking it again. To measure i_1 accurately is not quite so easy. The most obvious way to do so is to connect B to P and measure the total current received by the whole of the lower part of the apparatus. But it was found that, in order that the rays striking P should be homogeneous in speed, and all have the speed $V = V_1 - V_2$ it was necessary that V_2 should be not less than 40 volts, and in a direction to retard the rays entering B. (That is to say, besides the rays of speed V_1 entering B, there are some others of a speed between 0 and 40 volts, which probably represent the result of the ionization of A by the rays falling on it.) But if the tube projecting from A into B is at a potential considerably higher than P or B, many of the rays leaving P will be attracted to the tube, instead of to B, and the current

received by B and P together will be less than the whole current entering B. Another way of measuring i_2 is to prevent any of the rays leaving P by making U sufficiently large and positive ; it is obvious that if B is kept connected to W none of the rays from W either before or after striking P will strike B* ; all that enter B must come to rest finally either on P or on the tube, and very few will strike the tube after striking P because the tube is surrounded by metal which repels the rays. This method of measuring i_2 is much more satisfactory than the other, and was always adopted ; but it must be noted that, unless the rays entering B have all exactly the same velocity the number striking P will not be the same when i_1 and when i_2 are being measured. For the potential of B determines the potential at the mouth of the tube by which the rays enter ; when i_2 is being measured the rays are entering against a retarding potential $V_2 - 20$; when i_1 is being measured the retarding potential is V_1 and is always greater. But since it was found that the total current measured in this way did not vary by as much as 10 per cent. when the speed of the rays was varied (by means of V_2) from 400 volts to 2 volts, there is probably little uncertainty on this account, not enough at any rate to affect the conclusions it is proposed to draw.

The Changes in the Ionization.

3. It appeared that any change in P which reduced the value of the ionization for one speed of the incident rays reduced it for all speeds, so that in considering the nature of such changes we can speak of "the ionization" without reference to the speed of the incident rays. The precise variation of the ionization with the speed will be considered later.

Experiments were made with four metals : platinum, nickel, copper, and aluminium. In the cases of platinum and copper the changes were made both by heating the metal by an electric current and by making it the electrode of a discharge. In the earlier experiments on platinum and nickel the apparatus shown in fig. 1 was enclosed in a vessel constructed entirely of glass and protected from vapours by a U-tube cooled in liquid air. In the later experiments the apparatus was exposed to the vapours of sealing-wax, tap-grease, and mercury. No difference between the two arrangements could be found with platinum and nickel ; it

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* For reasons which it is needless to set forth in detail, B had to be at a slightly lower potential than W when V was small.

is assumed that none would have been found with copper or aluminium.

The changes produced by making the metal the cathode of an electric discharge were of precisely the same nature as those produced by heating in both the metals on which the effect of both procedures was tried (platinum and nickel). But the changes could be effected much more rapidly by means of the discharge. The lowest ionization that has been observed (in copper) was produced from state A by the passage of a discharge for only 5 minutes ; to produce state B from state A by heat always required about 24 hours, and even after heating for 300 hours (when an ionization as low as that mentioned had not yet been attained) decrease was still in progress. But whereas further heating always produced a decrease, the passage of a discharge sometimes produced a slight increase. The extent to which the ionization could be reduced appeared to depend mainly on the pressure of the gas through which the discharge passed ; the discharge appeared to be most efficient at a pressure of about 2 mm. of mercury, and its efficiency appeared to be closely connected with the amount of " sputtering " which occurred. Moreover, it did not seem to matter whether the plate was made the anode or the cathode of the discharge, but on this point I cannot be certain ; for though a valve-tube was included in the circuit, the form of the electrodes between which the discharge passed (B and P) was such that, at the pressure at which the discharge was most efficient, P acted as the cathode much more readily than B. It may be that P was acting sometimes as cathode even when the valve-tube was arranged so that it should act as anode. The discharge acted in the same manner whether the gas through which it passed was air, oxygen, hydrogen, or petrol vapour.

To illustrate the nature of the changes one series of observations may be given in some detail. The metal was copper and the value of R, taken as a measure of the ionization, was that corresponding to incident rays with a speed of 280 volts. When the metal was first inserted, after the surface had been polished by emery and oil, and heated to drive off the oil, R was 2·44. The passage of a discharge in 2 mm. of air for 5 minutes changed R to 0·89. Bombardment with cathode rays from W in a very high vacuum (current carried by rays about 10^{-5} amp. ; speed 150 volts) for 2 hours increased R to 1·42 ; further treatment of the same kind for 22 hours increased R to 1·623 ; further treatment for 52 hours left R unchanged at 1·621.

The discharge in petrol vapour for 10 min. reduced R to
1·115 : a further 15 min. increased R to 1·216 ; a further
15 min. reduced it to 1·187. Leaving the plate standing in
a mixture of petrol vapour and air for 72 hours increased R
to 1·209. A discharge in oxygen changed R to 1·369 ; a
further discharge to 1·097 and so on. Then the copper was
taken out and heated in a bunsen flame ; R became 2·39 ;
finally the surface was polished as at the start, and R returned
to 2·45.

These experiments and many others of the same kind lead
to the following conclusions with regard to platinum, copper,
and nickel. They are very similar to those announced
previously. There are two states of the metal, A and B,
which can always be reproduced. A is that produced by
polishing the surface with emery and (though with less
certainty) by heating it in a bunsen flame. In state A the
ionization is nearly the same for all three metals ; I found

$$Pt\ 2\cdot 38\ ;\ Ni\ 2\cdot 46\ ;\ Cu\ 2\cdot 44.$$

State B is that produced by reducing the ionization by
means of the discharge, and then restoring it as far as
possible by means of the bombardment of cathode rays in a
high vacuum. The ionization in state B varies notably
between the different metals ; I found

$$Pt\ 1\cdot 98\ ;\ Ni\ 2\cdot 22\ ;\ Cu\ 1\cdot 62.$$

The ionization can be reduced below that corresponding to
state B by heat or by the discharge. The lowest values I
have found are

$$Pt\ 1\cdot 203\ ;\ Ni\ 1\cdot 201\ ;\ Cu\ 0\cdot 888.$$

But I have not been able to find a method of reproducing
these values certainly, and it is not, therefore, by any means
sure that these are the lowest values which can be produced
or that there is a real difference between the three metals. It
will be noted that since in order to measure R it is necessary
to bombard the metal with cathode rays, it is quite im-
possible to measure accurately the lowest values of R.
Long-continued standing of the metal, whether in the most
complete vacuum that can be produced or in any mixture of
gases and vapours, produces a slight increase in R ; but the
variation in R which I have been able to produce by this
means is never so great as that which exists between the
actions of different discharges which are as similar as it is
possible to make them.

In aluminium the ionization in state A is much the same
as in the other metals ; $R = 2\cdot 60$. But by no action of the

discharge have I been able to reduce R lower than 2·31 ; I am not at all sure that this value corresponds to state B, because further action of the discharge increased R again to 2·47. The lack of alteration in aluminium by the discharge is doubtless connected with the absence of sputtering.

It will be observed that these conclusions agree in all but one respect with those advanced in the first paper. It has not been found, however, that state A can be regained from state B by bombardment with cathode rays in a high vacuum. It was thought that this result had been obtained because, in platinum and with the low speeds of the incident rays then employed, the ionization in state B does not differ very much from that in state A. Further experiments have shown that it does differ certainly, and that the only certain way to reproduce state A is to take the metal out of the tube and polish its surface. Long-continued standing in mixtures of gases or vapours has little or no effect.

4. There seems to be a simple and plausible explanation of these changes. We may suppose that the state A is that in which the metal is covered by a layer of gas, and that the state B is that in which this layer is removed. It is, of course, known that heat or the action of the discharge removes the layers of condensed gas adhering to the surface, and there are several lines of evidence which seem to show that the layer once removed is not easily restored. This idea would account for (1) the similarity of the values of R for different metals in state A ; (2) the methods of changing from state A to state B; (3) the difficulty of restoring state A, though perhaps the difficulty is rather greater than would have been anticipated. The reduction of the ionization below that corresponding to state B would then be due to some other change in the metal ; it might represent either a roughening of the surface by the sputtering and a consequent entanglement of the electrons liberated, or it might represent the effect of double-layers such as Seeliger has shown to exist. The second alternative is supported by the fact that the change is reversed by the action of cathode rays which Seeliger has shown to restore the double-layer removed by the discharge. It is difficult to suppose that the mere bombardment with cathode rays would have much effect in changing the molecular structure of the surface *.

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* The surface was examined with a microscope in states A, B, and in states giving less ionization than B. When the changes had been effected by the discharge the appearance of the surface was always different from that in state A, but no difference could be seen between the surface in state B and in the state giving less ionization than B.

It appears possible to test these ideas by quantitative measurements. If the change from state A to state B consists in the removal of the gas and the exposure of the metal, we should certainly expect in state B signs of an ionization potential different from that in state A. If, again, the changes beyond state B represent an increasing difficulty of emergence of the liberated electrons, then we should expect the ionization to be decreased in the same proportion, whatever the speed of the incident rays, for the speed of the liberated electrons is known not to depend upon the speed of the primary rays. Unfortunately, the quantitative experiments which have been made do not seem to support either of these ideas.

Variation of the Ionization with Speed of the Rays.

5. Fig. 2 gives some of the results which were obtained in a series of experiments with copper, no changes in the

Fig. 2.
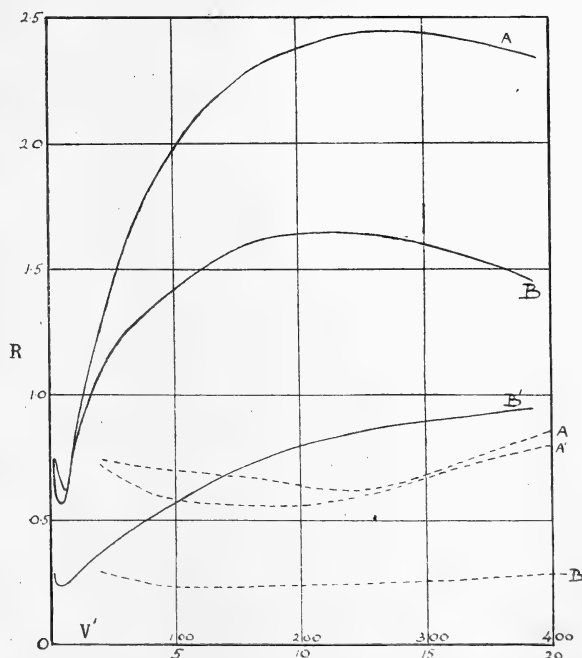
apparatus being made during the series except those effected by the discharge. These results are typical of all those obtained, except in a few particulars, which will be noted

explicitly. The continuous curves give the relation between R and V', the apparent speed of the rays, from 0 to 400 volts (upper row of figures on the abscissa), the dotted curves show the part corresponding to the smaller values of V' on a larger scale (the lower row of values on the abscissa). Curves A, B, B' refer respectively to the copper in state A, in state B, and in the state which gave the smallest ionization. 400 volts was the greatest speed obtainable with the source of steady potential obtainable ; some other observations were made with speeds up to 30,000 volts, the potential V_1 being obtained by an induction-coil, and V_2 being always 40 volts. These observations at higher speed will be noticed later.

An examination of the dotted curves would seem to show that the result announced in the first paper, that the ionization potential remained unchanged by the treatment to which the metal is subjected, is incorrect. In curve A, the minimum of R occurs at 12 volts, in B at 9 volts, in B' at 6 volts. And certainly the changes of this nature observed with copper are greater than those observed in the earlier or later experiments with platinum or in those with nickel. But since copper shows all the changes which are being investigated more markedly than the other metals, certain considerations have to be taken into account before concluding that this change in the position of the minimum really indicates a change in the ionization potential.

(1) The exact position of the minimum varies somewhat in different series. For state A values between 10 and 12 volts have been observed ; in state B values between 8 and 10 volts; in state B' values between 5 and 9 volts. It is clear, then, that the position of the minimum is not an exact indication of the ionization potential, and consequently that the progressive change of position of the minimum as the ionization is decreased may be capable of some other interpretation.

(2) The most probable of such interpretations would be based on a difference between V' and the true speed of the rays. V' is the difference of potential between W and P imposed by the battery; if there were at the surfaces of the metal other differences of potential, V' would not be the true speed of the rays striking P ; and, if these differences of potential varied, the same value of V' might correspond to different values of the speed. As was explained in the first paper, an attempt to allow for such differences of potential was made by observing the value of v, the potential between W and P when the current from P was

just zero; it appeared that the true speed of the rays should be $V' + v$. But I am by no means sure that the introduction of v really does give the true speed of the rays; v was very nearly constant (0·4 to 0·7 volt) throughout all the experiments; it varied very much less than would be expected from the known volta differences of potential between the metals employed. Moreover, the variation of v is certainly very much less than would be expected from the large values found by Seeliger for the potential differences in the "double-layers" which are produced at the surface of metals when cathode rays fall on them, and are removed by making the metal the cathode of a discharge. For nickel, Seeliger found potential differences as large as 20 volts. No change in v of this order of magnitude, and indeed no consistent variation of v with the state of the metal has been detected. Throughout the experiments no indication of the presence of such double-layers has been found; perhaps all the ionization investigated takes place at the outer surface of the layer; but even in that case a variation in v ought to be produced by its presence. I cannot suggest any reason why $V' + v$ should not give accurately the speed of the rays maximum falling on P.

(3) There is uncertainty arising from the difficulty of measuring i_1, which has been noted, but this source of error does not seem serious. An examination of the figures shows that unless i_1 actually increases as V_2 increases and V' decreases (such a change is almost inconceivable), an error in measuring i_1 could not account for the differences in the positions of the minimum. If i_1 falls more rapidly with V' than has been supposed, the difference in the position of the minimum would be increased and not decreased. Such an error may have been caused by the assumption, implied in the method of measuring i_1 adopted, that all the rays entering B fall on P, and that there is no appreciable scattering even at the lowest speeds. (It must be remembered that owing to the method of varying V' adopted, these low speeds would only be found close to P.)

A lack of homogeneity in the rays could hardly account for the variation of the minimum, for it is likely that such heterogeneity as existed would be the same in all experiments.

(4) The position of the minimum is determined, not only by the variation of the ionization with V' but also by the variation of the reflecting power. It is to be observed that the variation of the reflecting power at values of V' less than that required to produce ionization, does not agree with that found in the earlier experiments or with that found by

Gehrts. These other experiments indicated a maximum of reflexion at about 5 volts, which was especially marked in Gehrts' work. I am unable to explain this discrepancy. Gehrts' method of measuring i_1 was more satisfactory than my own, but in order to produce a maximum in my curves it would have to be supposed that i_1 had a maximum between 10 and 2 volts. On the other hand, the rays which I used in these experiments were probably more homogeneous than those employed by Gehrts or those employed in my earlier work.

Accordingly it does not appear to be at all certain that there is any change of the ionization potential with the treatment of the metal. If there is a change it consists of a reduction of the ionization potential as the ionization is decreased. And this result might seem in accordance with the idea that in state B the surface of the metal is exposed, whereas in state A it is covered with hydrogen. For it is to be expected that the ionization potential of metals should be less than that of hydrogen; the ionization potential of gaseous mercury is below 5 volts. On the other hand, if this explanation is adopted, it is not easy to see why the ionization potential should be reduced still further in passing from B to B'.

Careful comparative experiments have been made along the whole curve up to 400 volts; there is no indication whatever of any other kink in the curve suggesting the presence of an ionization potential greater than 12 volts.

6. Now let us turn to the part of the curve corresponding to greater values of V'. It is clear at once from the comparison of the curves B and B' that the expectation that, in the change from one of these states to the other, the ionization should be changed at all values of V' in the same proportion is not fulfilled. For whereas the maximum value of R occurs in B at about the same position as in A, in B' it occurs (if at all) at some much higher value. (The steady potential available was not great enough to determine the position of the maximum for B', but it appeared to occur between 400 and 9000 volts.) The following table gives the ratios of R (measuring the ionization) for different values of V' in the three states. For each value of V' the value of R in state B is put equal to 1; the figures corresponding to states A and B' are the ratios of the ionizations in these states to that in state B.

V'	40	80	200	300	400	9000	26000
R (state A)	1·16	1·35	1·45	1·52	1·62	1·61	1·66
R (,, B)	1·00	1·00	1·00	1·00	1·00	1·00	1·00
R (,, B')	0·36	0·38	0·49	0·56	0·67	0·79	0·87

It will be observed that the numbers corresponding to states A and B′ are by no means constant, and that there is a marked difference between the trend of the numbers in the two rows. In state B′ the ionization becomes more nearly equal to that in state B as V′ increases ; in state A it becomes less nearly equal to that in state B, though the ratio seems to tend to constancy (but not to equality) at the higher values of V′. These results seem to confirm completely the view that there is a marked difference between the state A on the one hand and the states B and B′ on the other, such as we might expect if in the state A the surface consists of a gas, and in the states B and B′ of the metal ; but I am unable to offer any explanation of the variation of the ratio of the ionizations in states B and B′ with the speed of the incident rays ; the change does not seem compatible with the view that the lesser ionization in state B′ is merely due to a greater opposition to the emergence of the electrons.

Some experiments were made in a completely different apparatus in which ionization at the surface of a nickel plate was produced, not by cathode rays, but by X-rays, or rather by the secondary cathode rays excited by X-rays. The experiments were difficult because of the smallness of the effect measured, but it was quite clear that by the passing of a discharge (and change from A to B or B′) the ionization at the surface was considerably decreased. The speed of the secondary cathode rays in these experiments, deduced from the absorbability of the X-rays, was about 50,000 volts. Accordingly, the difference between states A and B persists up to this speed.

7. Experiments were also made on the speed of the electrons liberated at the surface by the incident cathode rays ; they consisted of observations of the current flowing from P when the difference of potential between P and B was varied. If U is this potential (counted + when P is +), then the current is saturated if U is sufficiently large and negative or sufficiently large and positive ; in the latter case none of the electrons liberated at P leave P, in the former case all of them leave P. Let i_U be the current from P corresponding to the potential U. Then it is easy to see that, if there is no reflexion of the rays at the surface of B, $p = \dfrac{i_{+\infty} - i_U}{i_{+\infty} - i_{-\infty}}$ is the fraction of the rays liberated at P with a speed greater than U. For reasons which will appear presently, $i_{+\infty}$ was identified with i_{+20}, although the current was not completely saturated at this potential ; it

was completely saturated when U = −20. The presence of reflexion makes the absolute values obtained unreliable (it is due to this reflexion that the current is not saturated when U = 0, and that some of the rays appear to have a negative velocity), but it should not influence greatly the comparison of curves taken after different treatments of P.

The following table shows the results for nickel in states A, B, B'. V' in all cases was 400, but it appeared, as was expected, that so long as V' was considerably greater than 20, the form of the curve was independent of V'. The results with other metals were similar in all respects.

U	+20	+15	+10	+8	+6	+4	+2	+1	0	−2	−10	−20
p (state A)	0	·021	·065	·090	·121	·215	·358	·483	·708	·915	·992	1·000
p („ B')	0	·021	·075	·110	·159	·250	·417	·570	·732	·928	·991	1·000
p („ B)	0	·033	·087	·121	·186	·295	·500	·681	·811	·934	·991	1·000

These figures seem to indicate that, so far as there is any change in the speed of the rays, the speed increases as the ionization decreases—a conclusion which would be reconcilable with the view that the lower ionization is caused by a difficulty in the emergence of the electrons, so that only those with the greater speed emerge. But it must be remembered that, since the discharge is passed between P and B there may be a change in the reflecting power of B when the ionization is decreased; a decrease in the reflecting power of B with a decrease of ionization might also account for the apparent change in speed, for the number of rays leaving P and failing to return would be increased. The results which have been given show that the reflecting power of P for slow electrons is diminished greatly by the passage of a discharge, and since this change appears to be independent of the direction in which the discharge passes, it is probable that the reflecting power of B is actually diminished by the treatment that causes the decrease in ionization, and that the apparent change in the speed of the electrons is to be traced to this cause.

8. Some observations were made to determine whether the power of the metal to reflect incident rays with speeds greater than 40 volts was altered during the change from state A to B or B'; no such change is to be expected, for such reflexion probably takes place, not at the actual surface of the metal, but after the rays have passed through the surface. It is not, however, easy to determine the reflecting power for rays which are capable of producing ionization in

such an apparatus as was used. The electrons emitted in the process of ionization have practically all speeds less than 20 volts; the reflected electrons, when V' is greater than 40, have almost all speeds greater than 20 volts. Accordingly, it might be thought that the current carried by the reflected electrons would be measured by the change in the current flowing to P, produced by changing the potential difference between B and P from 20 to V' volts. But it must be remembered that when the reflected electrons fall on B they cause ionization there, and the electrons so emitted will be driven to P, so that by increasing the potential between B and P and preventing the reflected electrons from reaching B we may decrease and not increase the negative current received by P. And experiment shows that this effect is of importance, for at the higher values of V' i_{20}, the negative current received by P when $U = 20$ is actually greater than $i_{V'}$, that received when $U = V'$. The following figures give the ratio $i_{20}/i_{V'}$ for various values of V' in states A, B, B' corresponding to the three curves of fig. 2; if there were no reflexion the ratio would be 1; the occurrence of values greater than 1 indicates the effect of ionization at the surface of B :—

		40	80	120	160	200	240	280	320
	A	0·858	0·903	0·933	0·975	1·032	1·054	1·109	1·170
$\dfrac{I_{20}}{I_{V'}}$	B	0·835	0·894	0·913	0·953	0·976	1·010	1·039	1·067
	B'	0·921	0·918	0·920	0·919	0·920	0·945	0·956	0·997

At first sight these figures might seem to show that the reflexion is actually less in state B' than in state A ; but the difference between the figures can also be accounted for by supposing that it is not the reflexion, but the ionization produced by the reflected rays in B, which is the cause of the change.

It appears, then, that it is very difficult to interpret certainly the quantitative results in a manner to throw new light on the changes investigated. They seem to confirm the view that the state B does not differ from A merely as B' differs from B ; the change which produces B from B' is not a mere partial reversal of the change which produced B' from A. But they do not seem to decide without ambiguity whether the explanation of the changes proposed in § 3 is tenable. It is not certain whether there is a change in the ionization potential, and it appears that the decrease of the ionization between states B and B' must be due to

some cause more complicated than an opposition to the emergence of the electrons liberated, for this cause should produce the same proportional decrease whatever the speed of the incident rays.   But I have no further suggestion to make as to the nature of this change.

Summary.

The experiments described in a recent paper on "The Ionization of Platinum by Cathode Rays" have been extended to other metals and to higher speeds of the incident rays.

It is shown that the changes in the ionization which were found to take place on heating the platinum can be produced in that metal and in copper and nickel by making the metal one electrode of an electric discharge in air, oxygen, hydrogen, or petrol vapour at about 2 mm. pressure.   The changes were greatest in copper; in aluminium hardly any change could be produced.   The changes seem connected with "spluttering."

It appears that, in respect of this ionization, the surface of the metal can be in the following states :—(1) State A, which is that of the metal after it has been polished, (2) a series of states B' which are produced by the discharge. The ionization in the states B' is smaller for all speeds of the incident rays than in state A.   Of the states B', one, called B, is distinguished (1) because the ionization in that state is greater (for all speeds of the incident rays) than in any other of the states B', (2) because it can always be reproduced from any of the states B' by subjecting the surface to cathode ray bombardment.   State A cannot (as was stated previously) be reproduced from state B by such **treatment.**

It is uncertain whether the ionization potential in states B' is different from that in state A ; if it is different, it is lower.   It is also uncertain whether the speed of the electrons liberated varies with the state of the surface ; it does not vary with the metal (in state A) or with the speed of the incident rays.

The ionization produced by rays of any speed in a metal in the various states B' becomes more nearly equal and less nearly equal to the ionization by those rays in the metal in state A as the speed of the rays is increased.

It is suggested that the difference between state A and the states B' lies in the fact that in the former the metal is, and in the latter it is not, covered with a layer of gas.   If this explanation is correct, the ionization potential of a

metal may be less, but is certainly not greater, than that of hydrogen (11 volts). But on this view no explanation, consistent with the measurements, can be offered of the difference between the various states B'. It appears certain that these differences cannot be due to the presence of the " double-layers," the existence of which has been proved by Seeliger ; if such double-layers were formed at all in the conditions of these experiments, it seems that the ionization must take place at the outer surface of them.

Leeds, December, 1913.

XLI. *On the Law of Partition of Energy and Newtonian Mechanics.* *By* G. H. Livens [*].

VARIOUS attempts have been made, notably by Jeans [†] and Lorentz [‡], to prove that the only possible law of steady thermal radiation deducible from ordinary Newtonian mechanical principles is that which corresponds to equipartition of energy among the various oscillations, a law which is, however, totally in disagreement with the actual state of affairs as experimentally determined [§]. Ultimately these proofs reduce to the fact that equi-partition of energy among the various large number of coordinates of any dynamical system represents the only possible average partition which can reasonably be expected in any steady state.

It is therefore concluded that the Planck formula of radiation necessitated by experience is inconsistent with our ordinary mechanical principles, and therefore necessitates an essential modification in our usual stock of dynamical notions. Jeans even goes so far as to prove that the only

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[*] Communicated by the Author.
[†] Phil. Mag. Dec. 1910.
[‡] *Vide* A. Eucken, 'Die Theorie der Strahlung und der Quanta' (Halle, 1914).
[§] It is to be insisted that, although the equi-partition law apparently provides the right formula for long wave radiation, its application even in this part of the spectrum is open to certain objections. In pure thermal radiation, which presumably furnishes a continuous spectrum which would defy all attempts at resolution, the total number of different wave-lengths in any small range of extent $d\lambda$ even at the long wave-length end of the spectrum, is infinite, or at least must be assumed to be so in order to secure continuity of the spectrum. There would therefore be an infinite number of different oscillations which on the average secure the same finite amount of energy according to the equi-partition law. There would, therefore, be an infinite amount of energy associated with the small range $d\lambda$ in any part of the spectrum.

conceivable mechanical scheme which can lead to Planck's law is one in which elements of energy of a definite size play an important and essential part.

In a previous paper on the statistical theory of radiation, I have attempted to show that the application of certain tentative ideas in the statistical theories of both Planck and Jeans enable us to arrive at Planck's formula, but without any very unnatural assumptions. The ideas there tentatively introduced, which may appear rather crude and uncertain, involve a modification, not of our ordinary mechanical notions but merely of the one additional fundamental principle * that all dynamical coordinates which enter into the usual expression for the energy of any system are necessarily equally probable as receptacles of energy ; this modification † applies most particularly to those coordinates, infinite in number, introduced by the use of Fourier's series and usually expressed by the coefficients in these series.

It may well be asked, why is it that these coordinates are not equally probable, seeing that they all enter into the energy function in precisely the same way ?   But it may be equally well asked whether the mode of appearance in the energy function, or more generally in the dynamical theory, is sufficient criterion for the probability of the coordinate as a general receptacle of energy in any statistical problem. Besides the assumption that all the coordinates are alike in this one respect is nothing if not impertinent, seeing that it implies a good deal more knowledge of the higher order coefficients in the Fourier series than any mathematical theory would allow.   And after all the coefficients in the Fourier series are at least differentiated from each other by their places in the series, and I see no reason to suppose that their differences end at this.

If we are prepared to adopt such a modification of the theoretical bases of the statistical method in mechanics, it can be shown that the form of the theory which is to agree with experience is at least not inconsistent with our usual Newtonian mechanical notions.

We assume quite generally that the state of any dynamical system is determined at any instant by its state at the previous instant, and that this state can be specified by the value of certain definite generalized coordinates.   The motion

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* It is very important to recognize that this principle underlies all deductions of the equi-partition law, and is *additional* to the mechanical principles involved.

† A similar modification is implied in Planck's theory, but a dynamical reason, involving a discrete atomic structure for the energy, is assigned for it.

of the system between the two instants is presumed to be governed by the ordinary Newtonian system of mechanical laws, so that a general set of coordinates sufficient for our purposes would be provided in any set of generalized Lagrangian coordinates of the system $p_1, p_2, \ldots p_n$, and the momenta corresponding to these, say $q_1, q_2, \ldots q_n$. The equations of motion can be taken in any of the usual general forms.

If we construct a $2n$-dimensional space a single point in this space, namely the point whose coordinates are $p_1, p_2, \ldots p_n$; $q_1, q_2, \ldots q_n$, will represent the state of the system at any instant, and the general equations of motion are the equations to the paths or trajectories traced out in this space by the representative points as they follow out the different possible motions of the system. It is obvious that through every point in the generalized space there is one and only one trajectory, and that as a point moves along a trajectory and so follows the motion of a system, its velocity at any point depends only on the coordinates of the point and not on the time.

In the usual manner we can therefore imagine every region of the generalized space which represents a physically possible state of the system to be filled with so many representative points, that the whole collection of points may be regarded as forming a continuous fluid. The general equations of motion then assert that this fluid moves along fixed stream-lines and that the velocity at any point is constant. Moreover, we know from Liouville's theorem that if we follow the motion of all the points from the inside of any elementary parallelopiped

$$dp_{1_0} \cdot dp_{2_0} \ldots dp_{n_0} \cdot dq_{1_0} \cdot dq_{2_0} \ldots \cdot dq_{n_0}$$

at time t_0, they will be found at time t in the corresponding parallelopiped

$$dp_1 \cdot dp_2 \ldots dp_n \cdot dq_1 \cdot dq_2 \ldots dq_n,$$

and the volumes of these parallelopipeds are the same. The same is also true of the projections of the points on the elementary area $(dp_r dq_r)$ parallel to one of the coordinate planes defined by a generalized geometrical coordinate and its corresponding momentum, the area remaining constant.

The density of the fluid, or the density of the aggregation of the representative points thus remains constant throughout all time, so also does its density parallel to any $(p_r q_r)$ plane. The initial distribution of the density is entirely at

our disposal and may be chosen as simple as we like. The simplest and most convenient thing to do is to make it uniform throughout the whole of the space with which we are concerned.

This mass of fluid moving in the generalized space now provides a basis for the introduction of the calculus of probabilities ; but, as Jeans says, great care must be exercised in settling the basis for the calculation of the probability. Of course for our analysis to be legitimate we are not compelled to choose any one particular basis for the calculation of the probabilities. We may select any basis we please, and then the analysis will be legitimate if we retain the same basis throughout the whole investigation.

In the present instance we agree to state that the probability of the motion in any one type of coordinate, say p_r, being in any state A_r is, on some definite scale, measured by $f_r(a_r)$, where f_r is some, at present undetermined, function of its argument a_r, which is the area, measured in definite units, of the projection on the $(p_r q_r)$ plane of the volume occupied by points representing systems in which the motion in the p_r coordinate has the characteristic A_r : the relation between the probabilities for different types of coordinate are determined as soon as we know the form of the function f_r for each of them.

If we are dealing with a system, or part of a system, comprising an entirely large number of one particular type of coordinate for which the function f is the same (say m_r coordinates of type p_r), then we shall agree to say that the probability of this system being in a state A_r is

$$W_r = F_r(V_r),$$

F_r being some definite function of V_r, which is the volume occupied by the representative points for the system characterized by the state A_r. It is, however, important to notice that if the characterization of the state A_r is general and bears no reference to, or preference for any special members of the coordinate system, the only really possible functional forms for the functions f_r and F_r are such that

$$f_r(x) = c_r x^{\alpha_r}, \quad F_r(x) = C_r x^{\alpha_r},$$

where α_r is a constant, the same for all the coordinates of the specified type. This follows at once from the fact that in these circumstances the coordinates share equally, one with the other, the responsibilities implied in the specification of A_r, the probability that any coordinate is in the conditions

in which it can exist in the systems characteristic of the state A_r being the same for them all.

The procedure here adopted is more general than that adopted by Jeans inasmuch as it is not assumed that equal volumes in partial spaces corresponding to different types of coordinate are equally probable with each other.

Now consider a few generalities regarding a more complicated system comprising a large number of separate types of coordinates. Let A_1, A_2,...... be characteristics of different parts of the system, such that the coordinates involved in the specification of any one characteristic are not involved in any of the others and are in addition all of one specified type. Let W_1, W_2, ... be the respective probabilities, calculated on the predetermined scale, that in any random choice of a system from all those possible the respective parts shall possess the characteristics A_1, A_2, ... A complete system obtained at a single random choice may possess two or more of these characteristics simultaneously, and the probability that it possesses them all is of the form

$$W = W_1, W_2, W_3 \ldots\ldots$$

If we now put

$$S = k \log W,$$

then we know that S is proportional to Boltzmann's measure of the entropy of the system with the specified characteristics, probabilities now being measured on the basis provided by the generalized space as described above.

Now let E_1', E_2',... be the energies of those parts of the system with which the properties A_1, A_2, ... are associated and let E be the total energy given by

$$E = E_1' + E_2' + \ldots\ldots$$

The total entropy S is then given by

$$S = \Sigma\, k \log W_r.$$

Now the characteristics A_1, A_2,...... may be chosen so as to determine the partition of energy. To be precise let any characteristic property A_r be satisfied if the corresponding energy E_r' lies between $E_r - \frac{1}{2}\epsilon_r$ and $E_r + \frac{1}{2}\epsilon_r$. Let it be assumed as a property of the system that if left to itself it will assume a steady state in which the energy is divided in a definite manner, namely one in which E_r' becomes equal to the corresponding E_r at least to within the small range ϵ_r. Then W must be equal to unity for these values of E_1', E_2'. ......and this is its maximum value. It follows that S is also

a maximum when each E_r' is equal to the corresponding E_r, subject to the sum being equal to E. The analytical condition for this is, in the usual way, that all the E_r''s are given by the system of equations

$$\frac{\partial S}{\partial E_1'} = \frac{\partial S}{\partial E_2'} = \ \ldots\ldots$$

combined with the equation

$$E_1' + E_2' + \ldots\ldots\ \ = E.$$

If now we proceed on the basis suggested above and put

$$W_r = V_r^{\alpha_r},$$

we find that

$$S = \Sigma\, k \log W_r$$
$$= \Sigma \alpha_r k \log V_r,$$

so that

$$\frac{\partial S}{\partial E_r} = \frac{\alpha_r k}{V_r}\frac{\partial V_r}{\partial E_r}.$$

Now suppose that the first part of the system is a perfect gas. Its energy will be then simply the kinetic energy

$$E_1' = \Sigma\, lq^2,$$

the sum Σ here extending to say m_1 terms, all representing identical types of coordinates. In this case V_1 is the volume of the generalized space in which $\Sigma\, lq^2$ lies between $E_1 - \frac{1}{2}\epsilon_1$ and $E_1 + \frac{1}{2}\epsilon_1$, which is known to be of the form

$$V_1 = C_1 E_1^{\frac{1}{2}m_1 - 1}\epsilon_1,$$

wherein C_1 is a definite constant. Thus

$$\frac{1}{V_1}\frac{\partial V_1}{\partial E_1} = \frac{\frac{1}{2}m_1 - 1}{E_1},$$

which since m_1 is very large is practically the same as

$$\frac{1}{V_1}\frac{\partial V_1}{\partial E_1} = \frac{m_1}{2E_1};$$

so that

$$\frac{\partial S}{\partial E_1} = \frac{\alpha_1 km}{2E_1}.$$

But if θ denote the absolute temperature of the system in the steady state and R the usual absolute constant of gas

theory, E_1 is known to be equal to $\frac{1}{2}m_1R\theta$. Thus we have

$$\frac{\partial S}{\partial E_1} = \frac{\alpha_1 k}{R\theta};$$

or if we use $\alpha_1 k = R$ then we see that

$$\frac{\partial S}{\partial E_1} = \frac{\partial S}{\partial E_2} = \cdots \qquad = \frac{1}{\theta},$$

which is the general result expressed by the second law of thermodynamics.

The present considerations do not therefore affect the truth of the second law of thermodynamics, but this does not appear to justify us in the conclusion that the theorem of equi-partition is also true, as the following analysis shows.

Suppose that any other part of the energy, say E_2', can also be expressed in the same form as E_1', viz.

$$E_2' = \Sigma\, lq^2$$

the summation now extending to m_2 terms. The value of V_2 can then be calculated in the same way as V_1, and now we find

$$\frac{\partial S}{\partial E_2} = \frac{1}{\theta} = \frac{\alpha_2 m_2 k}{2 E_2} = \frac{\alpha_2}{\alpha_1}\frac{m_2 R}{E_2},$$

so that

$$E_2 = \frac{\alpha_2}{\alpha_1}\frac{m_2 R\theta}{2},$$

a resultant which is not consistent with the theorem of the equi-partition of energy since the average energy in this particular type of coordinate is now only $\dfrac{\alpha_2}{\alpha_1} \cdot \dfrac{R\theta}{2}$, and not $\dfrac{R\theta}{2}$ as in the case of the perfect gas, which forms part of the same system.

It would thus appear that if there is any reason to suppose that the various coordinates, and in particular the coordinates of the Fourier series, are to be differentiated from one another on the lines suggested above, then equi-partition of energy is hardly to be expected ; but any such differentiation in type, although not actually contained in our usual stock of dynamical ideas, is at least as consistent with these ideas as the usual assumption made regarding this point, so that there is every reason for adopting it as a useful, if arbitrary, additional hypothesis to replace the one already in use.

Applications in Radiation.—In attempting to apply the statistical principles of the preceding paragraph to the

fundamental problem in radiation, we should again fail to obtain anything like the definite radiation formula proposed by Planck, but the result obtained has now the additional advantage of being extremely indefinite. This indefiniteness is, however, not very surprising seeing that we know so little about the dynamics of the system concerned in radiation phenomena, and are therefore quite at a loss to determine anything about the constants α_r tentatively introduced in the above analysis, or even the total number m_r of the co-ordinates of any particular type. We do know, however, that for instance the possible vibrations, each of which presumably corresponds to a degree of freedom, of the type specified by the fact that the radiation from it has a wave-length lying in the infinitely small range between λ and $\lambda + d\lambda$, are infinite in number, but such knowledge is, under the present circumstances, worse than useless.

We are not, however, prevented from obtaining further information on this subject because there are still two methods of attack open to us. The first, or Planck's method, has been fully discussed in a previous paper, and the conclusion to be drawn from it is identical with that drawn in the previous paragraph, unless it is preferred to retain in the analysis the hypotheses of a finite limiting ratio between the elements of energy and extent of the elementary cells which form the bases for the application of the probability calculus, in which case it is possible to obtain Planck's formula. The suggestion that Planck's formula essentially involves an assumption of this kind and nothing else, is due to Larmor [*], but I am not yet aware of any plausible physical reason for it [†]; some such assumption is, however, necessitated by the requirements of definiteness in the ultimate formula, and it is not inconsistent with any of our usual stock of ideas, so that for the present, at least, something will be gained by retaining it.

There is yet another method of attack still open and this is the converse one followed by Jeans, but, contrary to the conclusion drawn by Jeans from his work, I cannot agree that anything very definite can be got out of it. The method exactly reverses the argument of Planck and starts with the assumption that his formula is correct. Let us therefore assume that in any given system in thermal equilibrium the

[*] Proc. Roy. Soc. vol. lxxxiii. 1909.

[†] I should like to take this opportunity of applying a reservation to certain remarks bearing on this question which were made in my previous paper. On due consideration of the various possibilities I think it will be difficult to avoid Larmor's suggestion, even if we cannot find a good reason for it.

components of the radiation with wave-lengths differing only infinitesimally from λ arise from the large number N of vibrators. Their total energy E must, according to Planck's law, be given by

$$E = \frac{N\epsilon}{e^{\frac{\epsilon}{k\theta}} - 1},$$

where $\epsilon = \frac{hc}{\lambda}$, h being Planck's constant. Eliminating the temperature between this and the equation

$$\frac{\partial S}{\partial E} = \frac{1}{\theta},$$

we get

$$\frac{\partial S}{\partial E} = \frac{k}{\epsilon} \log \left(1 + \frac{N\epsilon}{E}\right),$$

which gives on integration

$$S = k \left[\left(N + \frac{E}{\epsilon}\right) \log \left(N + \frac{E}{\epsilon}\right) - \frac{E}{\epsilon} \log \frac{E}{\epsilon} \right].$$

Thus on the usual bases of probabilities

$$\log W = \left[\left(N + \frac{E}{\epsilon}\right) \log \left(N + \frac{E}{\epsilon}\right) - \frac{E}{\epsilon} \log \frac{E}{\epsilon} \right],$$

whence using $P = \frac{E}{\epsilon}$ and with Stirling's approximation,

$$W = C \frac{(N + P)\,!}{P\,!}.$$

Thus on the basis of our previous measure of probability, we see that the space occupied by points representing the system with coordinates corresponding to these vibrations with their total energy between $(E - \frac{1}{2}\epsilon,\ E + \frac{1}{2}\epsilon)$ has a volume

$$V_N = \left[C \frac{(N + P)\,!}{P\,!} \right]^{\frac{1}{a_N}}$$

If we made ϵ infinitely small, as we should generally be entitled to do, this formula reduces to

$$V_N = C' E^{\frac{N}{a_N}},$$

unless of course $N\epsilon$ is comparable with E, in which case no such simplification is possible.

In any case, however, it appears to be quite impossible, owing to our lack of knowledge regarding both a_N and N, to

draw any conclusions regarding the volume of this space as compared with that discussed above, or the size of the element of energy which is used in the usual method of deducing this formula, or even the number of vibrations involved (which, however, on Planck's method, must have a finite limit). The equality of the spaces in the two cases would, however, imply some such relation as that discussed in our previous paper and mentioned above, between the element of energy and extent of cells.

In conclusion it might be useful to illustrate the restrictions and limitations of Planck's Theory by the alternative deduction given by Jeans.

Other things being equal, if a vibration can have energies $0, \epsilon, 2\epsilon, \ldots$, then the ratio of the probabilities of these events, as in the usual gas theory calculations, are

$$1 : e^{-2q\epsilon} : e^{-4q\epsilon} : \ldots : \ldots,$$

where, however, according to the calculations given in the earlier part of this paper, q is not equal to $\dfrac{1}{2RT}$ but to $\dfrac{\alpha_1}{2\alpha RT}$, α being the value of the probability constant corresponding to these vibrations.

If out of the N vibrations under consideration M have zero energy, then the number which have energy ϵ is $Me^{-2q\epsilon}$, the number having energy 2ϵ is $Me^{-4q\epsilon}$ and so on. Thus

$$N = M(1 - e^{-2q\epsilon} + e^{-4q\epsilon} + \ldots)$$
$$= \frac{M}{1 - e^{-2q\epsilon}}.$$

If E is the total energy of the N vibrations

$$E = M\epsilon(e^{-2q\epsilon} + 2e^{-4q\epsilon} + \ldots)$$
$$= \frac{M\epsilon e^{-2q\epsilon}}{(1 - e^{-2q\epsilon})^2} = \frac{N\epsilon}{e^{2q\epsilon} - 1},$$

which is Planck's law if

$$2q\epsilon = \frac{\alpha_1 \epsilon}{R\alpha\theta} = \frac{hc}{R\lambda\theta}$$

and

$$N\epsilon = \frac{Lhc}{\lambda}.$$

But now ϵ can be taken to be zero if α is sufficiently small and N sufficiently big.

It is perhaps worth while here emphasizing again the essential difference between Planck's formula and many interpretations of it. Although it is quite obvious that the only certain point about Planck's law is that the formula

$$\frac{c\bar{\epsilon}}{e^{\frac{\epsilon}{k\theta}} - 1} \cdot \frac{d\lambda}{\lambda^4}$$

expresses the energy per unit volume to be associated with the component of the radiation with wave-length between λ and $\lambda + d\lambda$, many authors interpret the theory in a manner that implies that the energy of a perfectly monochromatic constituent must be finite. Such a statement can, however, hardly be true, when we consider that ultimately an infinite number of such constituents are to be associated with any small range in the spectrum.

Conclusions.—In any case the general conclusion must be that Planck's law does not require or necessitate anything in the form of definite multiples of a fixed unit of energy, nor is it in this or in any other respect in contradiction with a general interpretation of the ordinary laws of Newtonian dynamics. It is not suggested that this formula does not involve anything but what can be derived from ordinary dynamical principles ; but it is insisted that any statistical considerations regarding dynamical problems do, in fact, involve an additional hypothesis over and above those provided in our usual dynamical schemes, and that therefore a modified form of this hypothesis cannot be said to be inconsistent with dynamical principles, since it has in reality nothing whatever to do with these principles.

The modification thus introduced into the theory involves merely a revision of the principles of the calculus of probabilities as applied in such problems. After all it is the method of application of this calculus which is most probably the vulnerable point in any statistical theory, so that it is hardly surprising that the new phenomena of radiation force us into new paths in this direction. While it is possible thus to shift the responsibility for the particular form of the theory necessitated by experience from the definite dynamical principles to the indefinite statistical ones, it would appear that no conclusions regarding the general applicability or otherwise of these principles can be drawn from the theory.

The only impression left by the foregoing discussion is rather one of indefiniteness. There appear to be so many indefinite constants in the theory, that it is difficult to draw any definite conclusions respecting any of the quantities

involved, such as those drawn by Planck and Jeans; although it appears that certain relations must exist between these constants if Planck's formula is to be obtained. Investigation seems to be necessary to attempt to fathom these relations between the constants of the theory, or are we to accept them as unfathomable properties of natural phenomena?

The University, Sheffield,
    November 4, 1914.

Note added Jan. 16th, 1915.—The main contention of the present paper is capable of explanation in terms of a well known difficulty in the ordinary statistical kinetic theories connected with the " continuity of the path " of a dynamical system. It is in fact definitely denied that a dynamical system which involves in its essential constitution a perfectly irregular mass of vibrating elastic matter (or æther) when started from any phase will traverse every other phase geometrically consistent with the energy condition. In fact, motions of the system in which more than a limited finite number of the higher vibration coordinates possess an amount of energy comparable with that of a dynamical coordinate of ordinary type (translation coordinate of a gas molecule, for example) are impossible both mathematically and physically.

XLII. *Displacements in certain Spectral Lines of Zinc and Titanium.* By Genevieve V. Morrow, *Ph.D., A.R.C.Sc.I.* (1851 *Scholar*)[*].

WITHIN recent years many observers claim to have found displacements in the lines of the arc and spark spectra of various elements, whilst others affirm that there is no alteration in the wave-lengths, and that the differences found have been caused by inaccuracy or by the methods used in measurement. Professors Exner and Haschek [†] have found displacements in certain lines of zinc and titanium by their method of measurement—that of projection on a divided screen. It seemed of interest to obtain, by means of the same apparatus which they had used, the arc and spark spectra of the same two elements, but under various conditions and methods of production, and to measure

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[*] Communicated by the Author.
[†] Exner and Haschek, *Sitzungsber. der Wien. Akad.* cxv. II. A. (1906) .

some of the lines by means of a micrometer. The present work has been undertaken to ascertain if under these conditions there is any displacement in the lines.

Rowland observed that the position of the iron lines in the sun's spectrum was not always constant, and the subject was further studied by Jewell [*], who found marked differences between the positions of the metallic lines in the arc and the sun. Humphreys and Mohler [†] noticed that increase of pressure in the arc caused metallic lines to be displaced towards the red, but that variation in the strength of the current did not affect the position of the reversals of lines. Mohler [‡] found corresponding results on lowering the pressure, but Duffield [§] noticed that reversed as well as bright lines were displaced towards the red, under increase of pressure in the arc. Jewell [‖] found that the stronger reversed lines were those whose displacement was greatest, and also that an increase in the arc in the quantity of material producing the line always displaced it towards the red, but an increase in the quantity of other material did not change the position of the line to the same extent, if at all. Kent [¶] compared the positions of the arc and spark lines with each other, and found that the part of the spark near the terminals gave lines the wave-lengths of which were greater than those of the arc, whilst those produced at the centre, where there is very little pressure, were not displaced, or only to a very slight extent. He suggests this as a reason for the fact that Eder and Valenta have observed no real displacements when comparing arc and spark spectra.

The question of the displacement of spectral lines is discussed by Exner and Haschek in their book ' Die Spektren der Elemente bei normalen Druck,' and their results show that the more intense a line is, the more strongly is it displaced towards the red. They found displacements of considerable dimensions in both arc and spark spectra, and in the bright as well as in the reversed lines. In another publication [**] they examined the spectra of the elements potassium, tin, and zinc under various conditions, and obtained displacements in the lines which in some cases were more than $0 \cdot 1$ Ångström unit, far beyond the region of error in

* Jewell, Astrophys. Journ. iii. (1896).
† Humphreys and Mohler, Astrophys. Journ. iii. (1896).
‡ Mohler, Astrophys. Journ. iv. (1896).
§ Duffield, Astrophys. Journ. xxvi. (1907).
‖ Jewell, Astrophys. Journ. iii. (1896).
¶ Kent, Astrophys. Journ. xvii. (1903) ; xxii. (1905).
** Exner and Haschek, *Sitzungsber. der Wien. Akad.* cxv. II. A. (1906).

the measurements. The displacements increased with the increase of the density of the glowing vapour. By a comparison of the arc and spark spectrum of the same element, they found that the wave-lengths in the spark were often less than those in the arc, but on the other hand the maximum displacement in the spark was the larger, which the authors attributed to the greater difference of density between the central and outer layers of the spark.

Amongst those who have found no displacement in spectral lines are Eder and Valenta [*]. They compared directly on the photographic plate the eight lines of zinc, in which Exner and Haschek had found displacements between arc and spark, but they could not observe any alteration in the position of the lines with respect to each other. They are of the opinion that an apparent displacement may be caused in a line by unsymmetrical broadening, but that the position of maximum intensity remains unaltered, and that the so-called displacements obtained by observers are caused by the measurements not being made through the most intense part of the line. Kayser [†] also has found no displacements in spectral lines, and suggests that the results of Exner and Haschek and those of Kent have been caused either by errors in measurement or by bad adjustment of the apparatus.

The spectral apparatus which was employed in the present investigation was the same as that used by Exner and Haschek in their experiments. In order to avoid the possibility of errors which might be caused by the projection method of measurement used by them, and of which Kayser did not approve, the plates were measured by means of a micrometer. This micrometer was constructed by Perreaux and permitted of measurements extending 30 cm. horizontally. It was of great importance to know if the thread of the screw was sufficiently fine and constant to permit of its being used in the present investigation, so the pitch was at first ascertained by the usual method. The distance travelled by the microscope along the screw was measured by focussing the cross-hairs on a divided millimetre scale of plated brass supplied by the Société Genevoise. This scale had been tested in Paris and found correct. Several sets of measurements were made and curves drawn to ascertain if the screw possessed periodic errors. The latter were not found, and the mean difference between the measurements of the pitch was ·0005 mm. Further measurements for finding the value

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* Eder and Valenta, *Sitzungsber. der Wien. Akad.* cxii. II. A. (1903).

† Kayser, *Zeitschr. für wiss. Photographie,* iii. (1905).

of the pitch were made in both directions along each centimetre of the screw, in order to avoid personal errors in the readings. The values found in seven sets of measurements varied between 0·4985 mm. and 0·4995 mm., so that 0·499 mm. was considered as being correct.

For the present work it was necessary to know the value of one turn of the screw in Ångström units. To ascertain this Professors Exner and Haschek kindly lent me a photographic plate of the spectrum of palladium, which had very sharply defined lines. The iron spectrum was on this plate as a standard, and the wave-lengths were taken from Rowland's tables. The palladium lines as well as 32 standards were measured, and the value of one turn of the screw in Ångström units was found from the standards. A curve was drawn taking the mean wave-length of each pair of standards as abscissa, and the corresponding factor for the screw as ordinate. This gave 1·3868 as a mean value for the factor. To ascertain how accurate the readings had been, the wave-lengths of the measured palladium lines were calculated. The differences between those found from this one measurement and those usually accepted as being correct did not exceed a few hundredths of an A.U. To test the accuracy of the readings further, the standards were measured in both directions, and the mean error for each reading was found to be 0·02038 A.U., which agrees very well with that obtained above. From five measurements in each direction for the same two lines, the mean error in one reading was found to be 0·0225 A.U.

From the above results it was evident that the micrometer was sufficiently accurate to detect a displacement of 0·04 A.U., which is the smallest recorded by Exner and Haschek.

The spectral apparatus consisted of a Rowland concave grating whose radius of curvature was 4·56 m.; it had 20,000 lines to the inch and 70,000 over the whole divided surface. The mounting of slit, grating, and camera was that of the well known arrangement of Rowland. The camera and grating are firmly bound together by a beam the length of which is equal to the radius of curvature of the grating, and they move on carriages along two rails which are set at right angles to each other, and above the junction of which the slit is situated.

The electrodes were held in clips which were so arranged that during the passage of the current they could be moved sideways, or their distance apart could be altered. For the production of the arc a direct current from 110 volts was

used, the strength being varied between 4 and 18 amperes by means of resistances. The alternating current which was used for the spark was furnished by a primary current of 25 amps. at 110 volts, which was transformed to a potential of 10,000 volts. In parallel with the spark was a Franklin condenser of 750 m. capacity. The distance between the electrodes in both arc and spark was from 4 to 5 mm.; and an enlarged image of the source of light was thrown on the slit by means of a Schumann condenser, which consisted of two crossed cylindrical quartz lenses—one being vertical and the other horizontal.

For obtaining the photographs Schleussner's orthochromatic Viridin plates were used. They were 30 cm. long and about 4 cm. wide and were placed in a curved position in the camera, so that they were on the circumference of a circle of 2·28 m. diameter. In this way the lines of the spectrum along the whole length of the plate were equally sharp. On each plate either the arc or the spark spectrum of the substance examined was photographed, and immediately below it and slightly overlapping it was taken the photograph of the arc spectrum of iron to be used as a standard. A vertical screen with a horizontal opening was placed before the camera so that only part of the plate was exposed at first, and it was then lowered the necessary distance before the iron was photographed, precautions having been taken that no possible displacement of the camera could occur between the two exposures. There were always common lines in both spectra due to some impurity, which could be compared in order to see if any accidental displacement had occurred, but in no case was such observed. The time of exposure for the arc spectra varied between 2 and 5 seconds, and in the spark spectra it reached a maximum of 5 minutes. The plates were developed with hydroquinone.

The wave-lengths of the standard iron lines were taken from Rowland's tables, and were so chosen that each line of the substance investigated could be referred to four well defined standard lines, that is to two on either side of it. Each plate was measured ten times,—five times forwards and five times backwards, and the mean of these measurements taken to calculate the wave-length. Two values were obtained for the wave-length of each line, one from each pair of standards near it, and the mean of these two values was taken as being correct. The difference between these values was in most cases only a few thousandths of an Ångström unit, but in a few instances it reached 0·025 A.U., that is

the mean error in measurement. For each line always the same standard iron lines were used.

The tables which are given below contain the results of the measurements of seven lines of the zinc spectra and thirteen lines of the titanium spectra. The first column contains the wave-lengths obtained in the arc by using pure metal electrodes and a current of 4 amperes. In the remaining columns the decimal of the wave-length is given which was obtained under the conditions stated at the head of the column. The numbers in brackets ( ) represent the intensities of the lines valued from 1 to 100, the greater number corresponding to the greater brightness. R means that the line is reversed, and *n* that it is not sharp. The wave-lengths obtained by Exner and Haschek are given in the last two columns of each table for comparison. Their scale of intensity is from 1 to 1000, *u* means the line is reversed, and + that it is not sharp.

Zinc.

Tables I. and II. contain the measurements obtained for the zinc lines.

The zinc which was used for the electrodes was the chemically pure zinc of commerce. For the spark the electrodes were about 2·5 cm. long, and 0·5 sq. cm. cross-sectional area with chisel-shaped edges, which were placed parallel to each other. The spark was vertical and parallel to the slit. Many photographs were taken of the spark spectra in the region of the lines chosen for examination, the time of exposure of the plate being varied from 2 seconds to 3 minutes. In this manner some plates were obtained having strong broad lines and others with sharply defined lines. Photographs of the arc spectra of zinc were also obtained, but some difficulty was experienced, owing to the lower electrode melting and falling away. This was avoided by melting some zinc into a small carbon cup and using this as the lower electrode. In order to ascertain the effect on the wave-lengths of the lines caused by alteration of the strength of the current in the arc, photographs of the spectra were taken when the current had various strengths between 4 and 18 amperes, the time and exposure being kept constant. In order to obtain lines of various intensities photographs were taken also when the time of exposure was varied. It was difficult to obtain weak but sharp zinc lines owing to the short exposure necessary, consequently part of the Schumann condenser was cut off by a screen, and thus only some of the light was allowed access to the slit.

TABLE I.

| | ZINC | | | | | BRASS | | | | | | Measurements by Exner and Haschek | |
	Arc		Spark			Arc			Spark			Arc	Spark
4 amperes.	17½ amps.	18 amps.	2* secs.	30 secs.	9 amps.	14 amps.	18 amps.	2 secs.	30 secs.	2 mins.		Arc.	Spark.
3345·699 (2)	·702 (40) R	·687 (70) R	·731 (15)	·756 (25)	·697 (10)	·703 (100)R	·751 (100)R	·726 (3)	·804 (10)	·796 (15)	{ ·70 (1) / ·78, 50)r	·71 (50)
3345·171 (3)	·163 (40) R	·173 (80) R	·211 (20)	·207 (30)	·155 (15)	·157 (100)R	·202 (100)R	·209 (4)	·253 (15)	·229 (20)	{ ·16 (2) / ·21(100)+u	·20 (300)
3303·044 (2)	·066 (35) R	·071 (70) R	·035 (15)	·083 (25)	·037 (10)	·049 (95)R	·115 (95)R	·121 (3)	·142 (12)	·139 (10)	{ ·10 (1) / ·16(100)+u	·10 (100)
3302·684 (2)	·698 (35) R	·686 (70) R	·724 (15)	·739 (25)	·656 (10)	·713 (95)R	·752 (95)R	·745 (3)	·788 (12)	·776 (10)	{ ·74 (1) / ·81(100)+u	·75 (200)
3282·468 (2)	·460 (40) R	·462 (75) R	·476 (15)	·498 (25)	·429 (10)	·498 (90)R	·505 (90)R	·496 (2)	·565 (8)	·525 (10)	{ ·46 (1) / ·50(100)+u	{ ·42 (8) / ·49 (100)

* Exposure.

TABLE II.

| | ZINC | | | | | BRASS | | | | | Measurements by Exner and Haschek | |
	Arc			Spark		Arc			Spark		Arc.	Spark.
4 amperes.	12 amps.	18 amps.	30 secs.	3 mins.	10 amps.	17 amps.	18 amps.	2 mins.	5 mins.			
4810·766 (15)R	·741 (40)R	·768 (40)R	·807 (15)	·792 (50)	·766 (15)R	·746 (10)R	·744 (100)R	·724 (2)	·735 (4)	·76 (200)	{ ·77 (5) / ·85 (500)r
4722·355 (15)R	·357 (45)R	·356 (45)R	·382 (15)	·395 (50)	·539 (15)R	·335 (10)R	·337 (100)R	·308 (2)	·306 (4)	{ ·33 (1) / ·39 (200)	{ ·37 (1) / ·50 (500)r

In order to find the effect, if any, on the wave-lengths of the lines caused by the presence of impurities in the arc and spark, brass electrodes were used, which of course caused copper as well as zinc to be present in the glowing vapour. The electrodes had approximately the same dimensions as those of zinc. The arc and spark spectra were obtained under the same conditions as those of pure zinc, with the exception that in the case of brass of course there was no difficulty with regard to the melting of the electrode. The time of exposure was varied between 2 seconds and 5 minutes.

Table I. shows that by using a current of 4 amperes the arc spectrum of zinc gives wave-lengths for three of the chosen lines $\lambda\lambda$ 3345·6, 3345·1, 3282·4, which correspond fairly well with those given by Exner and Haschek when the lines have about the same intensity; but the wave-lengths for the lines λ 3303 and λ 3302 are not so great as theirs, and even the greatest values obtained for these lines in the present work are not so large as those of the strongest lines of Exner and Haschek. The wave-lengths here given for these two particular lines when 4 amperes current is used correspond more nearly with the values λ 3303·03 and λ 3302·67 given by Eder and Valenta. An increase in the strength of the current to 17 or 18 amperes seems to have no effect on the wave-lengths of the lines, within the limits of error, although the intensity of the lines is greatly increased, and they are all reversed. In the spark spectrum obtained from 2 seconds' exposure all these lines except λ 3282 appear to experience a displacement when compared with the previous arc measurements, and in each case the displacement is towards the less refrangible end of the spectrum. When 30 seconds' exposure was used all the lines showed a displacement towards the red when compared with the previous arc measurements.

In the arc spectrum of brass obtained by using 9 amperes current, the zinc lines show no displacement when compared with those of pure zinc from 4 amperes current, with the exception of λ 3282, the wave-length of which is smaller than with pure zinc. With a current of 14 amperes all the lines are reversed and the lines λ 3302 and λ 3282 are displaced towards the red, and with 18 amperes there is a considerable increase in the wave-lengths of all the lines. The fact that these reversed lines experience a displacement is in agreement with the results of Duffield, Jewell, and Exner and Haschek. The spark spectrum of brass obtained by giving

2 seconds' exposures gives lines which show a great displace-
ment towards the red when compared with those of the arc
spectrum of brass when a weak current is used.   With an
exposure of 30 seconds the displacement is increased in all
the lines, which is still the case on exposing for 2 minutes;
but in the latter case the line $\lambda\,3282$ has not such a large
wave-length as with an exposure of 30 seconds.

Table II. contains the measurements of the zinc lines
$\lambda\,4810{\cdot}7$ and $\lambda\,4722{\cdot}3$.

There is no displacement observed in the arc spectra with
increase of current when pure zinc electrodes are used,
which was also the case with the other zinc lines previously
examined.   Both lines are reversed with a current of 4
amperes, and although the lines are nebulous when 12 and
18 amperes are used, still the reversed part is in every case
quite sharp and easy to measure.   Eder and Valenta give
$\lambda\,4810{\cdot}71$ and $\lambda\,4722{\cdot}26$ as the wave-lengths of these lines,
which are considerably smaller than those given by Exner
and Haschek.   In the spark spectra there is a displacement in
each line towards the red when compared with the arc spectra;
the differences between the measured wave-lengths for each
line for the two different exposures lie within the limits of
error in measurement.   The limit which has been taken
above for displacements is reached for one line by an ex-
posure of 30 seconds, for the other by 3 minutes' exposure.
Both lines are unsymmetrically broadened towards the red,
the darkest part of the line in each case being almost on the
edge of the violet side, whilst the line itself gradually shades
off to the red.   The increase in the time of exposure pro-
duced no alteration in the measured wave-lengths.

The wave-lengths obtained for these two blue lines of zinc
when the arc spectrum of brass was photographed, showed
practically no deviation from the wave-lengths given by pure
zinc.   Even when the current is increased to 18 amperes
there is no change in the wave-length, which is contrary to
the results obtained from the five lines described above.   In
the table it will be noticed that there is a great difference
between the intensity of the lines when 17 and 18 amperes
current were used, which is accounted for by the fact that
there was a screen before the condenser lens in the one case
which cut off part of the light from the slit.   From this it
can be seen that the change in intensity causes no difference
in the wave-lengths obtained.   On using a current of 18
amperes the lines were very broad but the reversals were quite
sharp.   The spark spectra obtained from brass electrodes

give lines the wave-lengths of which are much smaller than those given by the arc spectra of brass or of pure zinc.

It may be seen that in no instance in the spark spectra of either pure zinc or brass do the lines $\lambda\,4810$ and $\lambda\,4722$ attain the maximum values given by Exner and Haschek, that is $\lambda\,4810 \cdot 85$ and $\lambda\,4722 \cdot 50$ respectively, although the lines show a displacement in the spark spectra of pure zinc compared with those of the arc.

Titanium.

The following table contains the measurements of the titanium lines.

To obtain the arc and spark spectra of titanium, pieces of the metal about the size of a pea were placed in the electrode clips and the current passed between points which had been set opposite to each other. The spark was in each case vertical and parallel to the slit. Many photographs of the spectra were taken, the time of exposure in the case of the spark being varied between 2 seconds and 1 minute, and in the case of the arc the strength of the current was varied between 4 and 18 amperes. In order to study the influence on the wave-lengths of the titanium lines due to the presence of other elements in the arc and spark, titanium potassium fluoride was used. This salt was dissolved in hot nitric acid which deposited a gelatinous precipitate on cooling, but this went partly into solution on shaking. Carbon electrodes were used, and some of this solution of the titanium salt was placed on the lower one. Then photographs were taken of the spark and arc spectra, varying the time of exposure and the strength of the current as with the metallic electrodes. As there were no titanium lines obtained by this means in the arc spectrum when a current of 4 amperes was used, a paste of the salt was made with water, and some of this was placed on the lower electrode, and by this method some lines of weak intensity were produced. On increasing the strength of the current more lines appeared on the plate, but with 18 amperes the salt, which seemed to be driven away from the region of the spark, melted and ran down the side of the electrode, so that no titanium lines appeared on the photograph. The thirteen titanium lines which were chosen for the investigation lie between $\lambda\,4000$ and $\lambda\,3300$.

TABLE III.

	Titanium Metal				Titanium Potassium Fluoride.				Measurements by Exner and Haschek.	
	Arc.		Spark.		Arc.		Spark.		Arc.	Spark.
4 amperes.	9 amps.	18 amps.	3 seconds.	1 minute.	4 amps.	11½ amps.	3 mins.	5 mins.		
3958·337 (3)	·377 (9)	·389 (15)	·360 (1)	·403 (8)	·397 (4)	·378(10)R*n*	·359 (1)	·376 (2)	{ ·35 (2), ·39 (15)	·39 (5)
3948·827 (2)	·840 (8)	·843 (10)	...	·892 (6)	·877 (3)	·861 (9)	·893 (1)	·903 (1)	·82 (1), ·87 (12)	·80 (4)
3913·609 (1)	·664 (6)	·667 (8)	·732 (2)	·699 (10)	...	...	·721 (2)	·702 (1)	·68 (5)	{ ·61 (2), ·72(20)
3904·936 (2)	·973 (6)	·987 (8)	...	·988 (6)	·939 (3)	·987 (8)	·951 (1)	·942 (1)	{ ·95 (1), ·99 (10)	·98 (5)
3900·688 (2)	·705 (6)	·729 (8)	...	·747 (20)	...	...	·702 (2)	·702 (1)	·72 (5)	{ ·70 (2), ·81(50)
3741·185 (2)	·207 (6)	·267 (10)	...	·235 (10)	·229 (4)	·260 (9)*n*	·196 (2)	·210 (2)	{ ·21 (1), ·25 (15)	·20 (2)
3685·310 (4)	·319 (8)	·376 (15)	·348 (4)*n*	·364 (30)	...	·375 (?)	·316 (5)	·321 (5)	·37 (8)	{ ·32 (5), ·37(100)
3641·484 (1)	·486 (4)	·540 (8)	·544 (1)	·539 (20)	...	...	·477 (2)	·463 (2)	·50 (3)	·49 (1), ·55(10)
3505·021 (2)	·030 (5)	·066 (9)	·046 (3)	·078 (25)	...	·048 (1)	·023 (4)	·032 (4)	·06 (3)	{ ·06 (3), ·10(30)
3383·862 (4)	·910 (6)	·966 (10)	·896 (4)	·967 (30)*n*	...	·938 (4)	·876 (6)	·882 (6)	·90 (3)	{ ·87(20)*n*, ·93 (3)
3372·908 (4)	·961 (3)	·968 (10)R	·968 (4)	·981 (35)*n*	·918 (1)	·965 (4)	·924 (6)	·935 (6)	·91 (4)	{ ·92(20)*n*, ·99 (5)
3349·532 (5)	·564 (8)	·560 (12)R	·577 (5)*n*	·644 (40)*n*	·531 (1)	·563 (4)	·538 (7)	·540 (7)	·56	{ ·52(10)*n*, ·61 (4)
3341·985 (4)	2·040 (6)	2·027 (10)R	2·068 (4)	2·063 (30)*n*	2·001 (2)	·980 (5)*n*	·989 (6)	·975 (6)	42·01	{ 42·00(10)*n*, ·09 (3)

The first column in Table III. gives the wave-lengths of the thirteen titanium lines in the arc spectrum obtained by using a current of 4 amperes and metallic electrodes. As may be seen the intensities of these lines are small, but they are well defined and sharp. The lines λ 3958·3, λ 3948·8, λ 3904·9, λ 3641·4, λ 3372·9, λ 3341·9 correspond fairly well with the wave-lengths given by Exner and Haschek when the lines have about the same intensity, but the other lines show a smaller wave-length than theirs, this being especially the case with λ 3913·6, λ 3900·6, λ 3685·3, and λ 3383·9. The wave-lengths given here for λ 3900·6 and λ 3685·3 correspond with the measurements of Eder and Valenta which are λ 3900·68 and λ 3685·30, those of Exner and Haschek being λ 3900·72 and λ 3685·37 respectively. The other lines λ 3913 and λ 3383 are not given at all by Eder and Valenta. When the strength of the current is increased to 9 amperes, most of the lines show an inclination towards the side of greater wave-length when compared with those obtained from a current of 4 amperes, but a decided displacement is seen in the lines λ 3958, λ 3913, λ 3904, λ 3383, λ 3372, and λ 3341, and in each case towards the red end of the spectrum. On further increasing the current to 18 amperes, all the lines are displaced more than 0·04 A.U. from the previous measurements with a current of 4 amperes, except λ 3948 and λ 3349, although the wave-lengths of each of these is greater than with 4 amperes. The lines λ 3372, λ 3349, and λ 3341 are reversed.

In the spark spectrum obtained by an exposure of three seconds, nine of the chosen titanium lines appear on the plate, and all show a displacement towards the red when compared with the corresponding lines obtained from the arc using a current of 4 amperes, although the intensities are almost the same in each case. The line λ 3913 was difficult to measure owing to the proximity of a line in the iron spectrum, but the alteration in the relative positions of the two lines can be seen even on examination of the plates with the naked eye. When the time of exposure is increased to 1 minute all the thirteen lines are seen on the plate, and all show a displacement of more than 0·04 A.U. when compared with the arc spectrum from a current of 4 amperes. The lines λ 3383, λ 3372, and λ 3341 are not sharp except at the ends, which part was measured in each case. The line λ 3349 is broad, and owing to the proximity of another titanium line equally broad, was difficult to measure.

Only seven of the chosen lines appear in the arc spectrum of titanium potassium fluoride when a current of 4 amperes

is used. The lines $\lambda\,3958$, $\lambda\,3948$, $\lambda\,3741$ show a displace-
ment towards the red when compared with the arc spectrum
of the pure metal obtained with the same current. None of
the other lines give smaller measurements than those obtained
from the pure metal under the same conditions. On in-
creasing the current to $11\frac{1}{2}$ amperes all the lines appear
except $\lambda\,3913$, $\lambda\,3900$, and $\lambda\,3641$. The lines $\lambda\,3958$,
$\lambda\,3904$, $\lambda\,3741$, $\lambda\,3685$, $\lambda\,3383$, and $\lambda\,3372$ all show a dis-
placement of more than $0\cdot04$ A.U. towards the red when
compared with the arc measurements of the pure metal with
a current of 4 amperes. The line $\lambda\,3948$ is increased in
wave-length by $0\cdot034$ A.U.

In the spark spectrum obtained from titanium potassium
fluoride all the lines appear when the plate is exposed for
3 minutes, and most of them have greater wave-lengths than
the corresponding arc lines of the pure metal obtained from
a current of 4 amperes. There is a distinct displacement
towards the red in the lines $\lambda\,3948$ and $\lambda\,3913$. If the
exposure is increased to 5 minutes the lines experience very
little alteration in wave-length, the differences being within
the limits of error in measurement. But when the results
of the spark measurements obtained from the titanium salt
and those from the pure metal are compared, it is noticed
that in some cases the pure metal gives lines the wave-lengths
of which are greater than those of the salt. This is the case
in the lines $\lambda\,3900$, $\lambda\,3685$, $\lambda\,3641$, $\lambda\,3505$, $\lambda\,3383$, $\lambda\,3372$,
$\lambda\,3349$, and $\lambda\,3341$. The same effect is observed with the
zinc lines $\lambda\,4810$ and $\lambda\,4722$.

Conclusion.

The foregoing measurements prove without doubt that the
wave-lengths of the lines in the spectra of the metallic
elements are not constant, but that they experience displace-
ments towards the red under certain conditions.

The wave-lengths of lines in the spark spectrum of the
pure metal are in general greater than those in the arc
spectrum, but the difference alters for the various metals
and for the different lines of the metals.

In the arc spectrum of the pure metal the lines are dis-
placed by increasing the current, if the point at which the
element vaporises be high enough for the increase in current
to produce an increase in the density of the vapour.

The presence in the arc or spark of atoms of another
element appears to have no influence on the wave-lengths of
the lines of the substance being examined, the wave-lengths
obtained depending on the partial density of the substance
itself.

The measurements show clearly in many cases that through over-exposure of the plate errors may be produced in the results, since on increasing the time of exposure, and consequently increasing the precipitate of silver on the plate, an apparent alteration can be found in the wave-length of lines which are unsymmetrically broadened.

The present research has been carried out at the Physical Institute of the University of Vienna. I take this opportunity of expressing my best thanks to Hofrat Professor Exner and Professor Haschek, at whose suggestion the work was undertaken, for their active interest and helpful criticism during its progress.

May 23, 1914.

XLIII. *The Relation between certain X-ray Wave-lengths and their Absorption Coefficients.* By W. H. Bragg, *D.Sc., F.R.S., Cavendish Professor of Physics in the University of Leeds* [*]

IN the figure is shown the X-ray spectrum of rhodium, in the second order, given by the (111) planes of calcite. The abscissæ denote the glancing angle, that is to say the angle between the incident X ray and the crystal

Fig. 1.
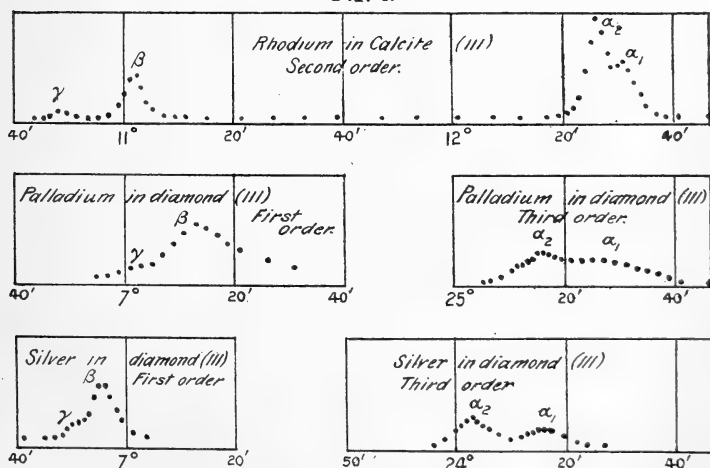
planes. The ordinates represent the readings of the electroscope attached to the X-ray spectrometer. In determining this spectrum, readings were taken every two minutes of arc, and every minute in the important regions. Each dot in the figure represents a separate measurement, but only

a few of the readings taken in the regions between the " lines " and on either side of them are shown in the figure. It will be observed that the spectrum is practically a pure line-spectrum. In fact, no general or " white " radiation can be found—a condition which is no doubt due to a particular state of the bulb. The small readings of the figure, which lie between the lines, are due to various minor causes, including scattering of X rays. If a diamond is employed, they are proportionally far less. With the spectrometer-slits opened to two or three millimetres so as to obtain the maximum effect, the electroscope-leaf moved 260 divisions in five seconds when the glancing angle (between incident rays and diamond) was $8°\ 30'$ and the reflected portion included the strong α line. When the angle was half this, the reading was not more than one division in the same time.

Calcite is an accurately built crystal, resembling diamond in this particular. It is a far better crystal for accurate work than rocksalt, which may be compared to a badly ruled diffraction-grating giving false images or " ghosts." The rhodium anticathode was placed so that the rays left it at a grazing angle, and the source of rays was therefore, in effect, a line parallel to the slits. The pencil of rays was limited just before incidence on the crystal by a slit $0\cdot2$ mm. wide. With this combination of circumstances, the lines of the spectrum are well separated from each other.

The spectrum contains four lines. The two of longest wave-length constitute the doublet which has already been observed and examined [*]. In combination they compose the strong line which Moseley [†] has observed to be given by a great number of substances, constituting in fact the principal part of the K series of characteristic radiations. The term " doublet" is not really justified, for there is no reason to suppose the two constituents stand in any special relation to each other. They may be spoken of separately as α_1 and α_2, which terminology will be in touch with Moseley's.

The line near to $11°$ in the spectrum is the other well-known constituent of the characteristic radiations of the K series ; it is known as the β line. There is also a fourth line which has not been noted before, so far as I am aware. It is marked γ in the figure.

Examination has also been made of the rays from bulbs having anticathodes of palladium and of silver. It was not

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[*] Nature, March 12, 1914; Phil. Mag. May 1914.
[†] Phil. Mag. April 1914.

possible to obtain such clear-cut results as in the case of rhodium, because the bulbs were of an old pattern and the anticathodes were surrounded by raised rims. The rays leaving at a grazing angle could not be used, and there was no longer a "line-source." The images were therefore blurred, more especially in the case of palladium.

Nevertheless the figure makes it clear that the spectra of all three metals are of exactly the same kind. Diamond was used instead of calcite in order to effect the separation of α_1 from α_2 by the use of the high resolving powers of the third order spectrum. In order to separate β from γ it was found best to use the first order spectrum ; the distance between β and γ is twice as great as that between α_1 and α_2, and the two can just be resolved in that order. In the third γ is too weak. It is certainly remarkable that the spectra of these three substances should resemble each other so closely. It will be of much interest to know how far the resemblance extends to the spectra of other substances.

The angle of reflexion of α_2 in the first order of calcite is $6° 11'$. The structure of calcite has been given by W. L. Bragg (Proc. Roy. Soc. lxxxix. p. 486). Assuming the density of the crystal to be $2 \cdot 71$ and the mass of the H atom to be $1 \cdot 64 \times 10^{-24}$, it can be calculated that the spacing of the $(1 \, 1 \, 1)$ planes is $2 \cdot 845$ A.U.

This gives

$$\lambda = 2 \times 2 \cdot 845 \times \sin 6° 11',$$

$$= 0 \cdot 613 \text{ A.U.},$$

agreeing well with the value $0 \cdot 614$ A.U. previously found by the use of diamond [*].

The values of all the wave-lengths in the three spectra may be readily calculated from the results illustrated by the figure. A value for the α line of Pd, $0 \cdot 576$ A.U. was given in a paper published in the Royal Society Proceedings, November 1913 ; the crystal used was rocksalt. Moseley [†], using potassium ferrocyanide calibrated by reference to rocksalt, found $0 \cdot 584$ for Pd and $0 \cdot 560$ for Ag. Recently Malmer [‡] gives for the α lines of Pd and Ag $0 \cdot 590$ and $0 \cdot 564$, and for the β lines of the same substances $0 \cdot 522$ and $0 \cdot 499$. He also used rocksalt. As far as the particular crystal has influence, diamond and calcite are to be preferred to rocksalt, for the reasons already given. The following table gives the wave-lengths in Ångström units calculated from the experiments described in this paper. The values

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[*] Phil. Mag. May 1914.   [†] Phil. Mag. April 1914.
[‡] Phil. Mag. December 1914.

for the γ line of Pd and Ag are not so reliable as the others.

<div align="center">TABLE I.</div>

	Ag.	Pd.	Rh.
a_1	0·562	0·589	0·619
a_2	0·557	0·583	0·614
β	0·495	0·516	0·545
γ	0·488	0·503	0·534

These measurements were undertaken in the attempt to throw some further light on the relation between wavelength and absorption in certain cases. Barkla has shown that in general the X rays characteristic of any substance are strongly absorbed by substances of lesser atomic weight as compared with substances of greater atomic weight. The phenomenon may be more definitely expressed in terms of wave-length. An instance is given in the table on p. 627 of the December (1914) number of the Philosophical Magazine. The β ray of silver (0·495 A.U., see the table above) is very strongly absorbed by Pd as compared with Sn or even Ag itself. Some figures given in the table quoted are reproduced here (Table II.) in slightly altered form, and will make the point clear.

<div align="center">TABLE II.</div>

X ray.	Log. of wave-length in A.U.	Log. of atomic absorption coefficient $\times 10^{22}$.	
		Pd.	Ag.
Ag β	$\bar{1}$·6946	2·064	1·260
Pd β	$\bar{1}$·7126	1·301	1·342
Rh β	$\bar{1}$·7364	1·350	1·394
Ag a	$\bar{1}$·7459	1·377	1·403
Pd a	$\bar{1}$·7657	1·452	1·477
Rh a	$\bar{1}$·7882	1·498	1·545

These are plotted in fig. 2. All the points representing the way in which the absorption of the different rays by

silver depends on the wave-length lie on a straight line within errors of experiment. This was to be expected more or less, because Owen has pointed out that the absorption coefficient by a given absorber varies inversely as the fifth

Fig. 2.

Log. (wave-length in A.U)
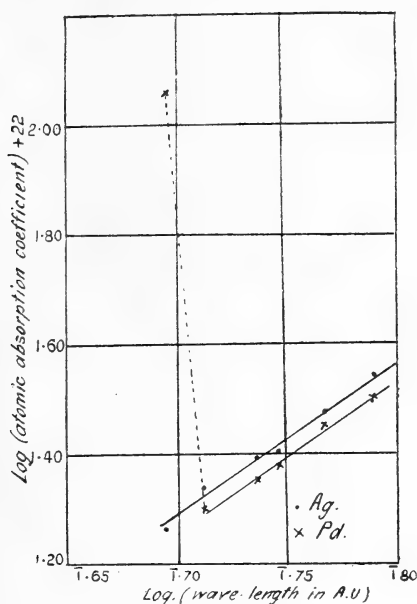
power of the atomic weight of the atom emitting the radiation, and we know that the latter, roughly, is inversely proportional to the square root of the wave-length which it emits. Consequently the absorption coefficient by a given absorber is proportional to (wave-length) , and logarithmic plotting should give a straight line. The slope of the lines in the figure gives an index 3 much more nearly than 5/2 ; but the range of wave-lengths in the table is too narrow for an exact deduction. Measurements of the absorption coefficients in terms of wave-length are being made over a much wider range, and will be useful in making a correct determination of the index.

If we consider the silver curve, we see that the absorption of the silver rays is not remarkable in any way ; the points for the silver wave-lengths lie on the straight line passing through the points for the wave-lengths of palladium and rhodium. Now it is certain that the high absorption which

occurs when a characteristic radiation traverses a substance of less atomic weight is accompanied by, and to some extent dependent upon, the production of secondary radiation. Zinc rays are highly absorbed by nickel, and at the same time zinc rays excite nickel rays. But nickel rays cannot excite zinc rays, and the absorption of nickel rays by zinc is relatively small.

When, therefore, we find that silver absorbs its own rays on no higher a scale than it absorbs those of Rh and Pd, which are of less atomic weight (the atomic weights of Ag, Pd, and Rh are 108, 107, and 103, their atomic numbers 47, 46, and 45), we conclude that none of the rays emitted by these three substances can excite any of the silver rays. This is the case although many of the waves are shorter than one or more of the characteristic silver waves.

If we examine the palladium curve, we find all things the same, except that the short silver wave 0·495 is highly absorbed by Pd, and no doubt excites Pd rays. Why should it be able to do so? It cannot be merely because it is shorter than some of the Pd waves, because the Pd wave 0·516 cannot excite Ag waves of greater length.

The most probable condition would seem to be that the exciting wave must be shorter than all the characteristic waves of the substance in which it excites those waves. It will be observed that the β ray of Ag is just shorter than the γ ray of Pd. Further examination of parallel cases will be necessary, of course, before this statement can be generalized. It seems likely, however, that certain peculiarities in Barkla's table of absorption coefficients can be explained by its aid. For example, Barkla states that the mass-absorption coefficients of Ni for the rays emitted by Ni, Cu, Zn are respectively 56·3, 62·7, 265. We should explain this on the ground that neither nickel ray can excite the characteristic rays of nickel, because of course neither is shorter than the shortest ; of the copper rays, one, the weaker, can excite the nickel spectrum and is highly absorbed, but the other, the longer and stronger, cannot do so and is not specially absorbed. The net result is that the copper rays, though shorter on the whole than the nickel, are nevertheless the more highly absorbed *as a whole*. Both the zinc rays can excite the nickel rays because both are shorter than the shortest nickel ray ; the zinc rays are very highly absorbed in consequence. It may be that the characteristic rays of a substance form a system which can only be excited as a whole.

XLIV. *On Condensation Nuclei produced by the Action of Light on Iodine Vapour. By* Harold Pealing, *M.Sc., Lecturer in Physics at South African College, Cape Town* *.

THE object of this research was to continue the investigation I carried out in collaboration with Professor Gwilym Owen, D.Sc. (an account of which we published in the Phil. Mag. for April 1911) ; and to test and examine the objections which Ramsauer made to the explanation we gave of our experiments.

From experiments we made with a Wilson's expansion apparatus it was shown :—

(1) That when light fell on a mixture of moist air or oxygen and iodine vapour contained in a freshly cleaned glass vessel, nuclei are produced possessing the following properties :

The nuclei are very unstable, disappearing in a few seconds in the dark, and carry no electricity and need oxygen and moisture for their production. The light required for their production need not be very intense, nor of a high degree of refrangibility. They usually reach their maximum size in less than one second, and as a rule they were not large enough to be caught by an expansion of less than 18·5 cm.

(2) No nuclei are produced after the iodine has been in the apparatus for some days, but if the apparatus was washed with nitric acid and finally with distilled water, nuclei reappeared.

(3) Glass-wool possesses the peculiar property of facilitating the formation of nuclei, the number produced when iodine-laden air is admitted into the apparatus through a plug of glass-wool being much greater than the number obtained on placing iodine directly in the cloud-chamber. This property becomes less and less marked as the wool becomes more and more saturated with iodine. We were unable to decide whether this action of the glass-wool was due to some impurity on its surface. In the case of the nuclei produced without the aid of the glass-wool, we were of the opinion that they were not produced by an impurity on the surface of the glass, but were produced by some chemical action between the iodine, water-vapour, and oxygen. To explain the disappearance of the effect we supposed that the chemical action was reversible, and that as soon as chemical equilibrium was established no more nuclei were produced.

The most conclusive evidence we put forward for this

explanation was that the effect reappeared every time the apparatus was carefully cleaned. When, however, the glass-wool (which had not been previously used) was cleaned, as far as possible in the same way, it gave an effect which was much less than it gave in the unwashed condition. Another important flaw in the evidence was the fact that when once the glass-wool had lost its property of producing nuclei, all attempts to bring back its property of producing nuclei failed. Obviously, as long as this was the case, the effects in the two cases being so similar except in actual amount, the evidence in favour of the explanation we gave could not be regarded as conclusive. For this reason the present investigation was carried out. Nearly all the experiments were with glass-wool.

Experiments with Glass-Wool.

First a word about experimental details.

(*a*) The apparatus used was very similar to the Wilson's apparatus used in the former experiments.

(*b*) The apparatus was not cleaned with extreme care as it was shown that the accidental impurities which glass gains when left exposed to the air have no influence on the effect investigated. The whole apparatus was thoroughly washed with a strong solution of soap and water and then carefully rinsed out with ordinary tap-water. Sometimes strong nitric acid was used before rinsing with the tap-water.

(*c*) The size of the nuclei was estimated by observing the pressure-fall in the Wilson's expansion apparatus necessary to bring them down. As a rule a pressure-drop of 18·5 cm. was necessary to catch the majority of nuclei, but very often a much lower pressure brought a large number of the nuclei down. The number of nuclei was estimated in a rough manner by finding out the density of the condensation cloud produced when an expansion was made, the expansion chamber of the apparatus being illuminated by the light focussed from a Nernst lamp.

(*d*) In order to eliminate causes other than the glass-wool of producing the nuclei, the apparatus was left standing with iodine in it until the effects produced on expanding the air contained were the same as those obtained before the introduction of the iodine. In other words, no experiments were made with the glass-wool until the apparatus gave, when saturated with iodine, the ordinary Wilson effects.

(*e*) The effect produced by the glass-wool was observed by passing iodine-laden air through a plug of it (about 25 cm. long) direct into the apparatus.

The table gives the results obtained when the plug was freshly set up.

A. Wilson apparatus containing moist dust-free air.		B. Wilson apparatus containing moist dust-free air freshly saturated with iodine vapour.	
Press. Fall.	Result (Ordinary Wilson Effect)	Press. Fall.	Result.
15·4 cm.	Nothing.	9·1 cm.	Nothing.
15·8 ,,	Few drops.	16·6 ,,	Thin shower.
17·3 ,,	Thin shower.	17·8 ,,	Good shower.
18·7 ,,	Good shower.	18·3 ,,	*Coloured cloud.*
19·7 ,,	Slightly tinted shower.		
20·3 ,,	Coloured cloud.		

C. Same as B. one day later.		D. Same as C, but iodine-laden air admitted through freshly set up glass wool plug.	
Press. Fall.	Result.	Press. Fall.	Result.
15·7 cm.	Few drops.	15·7 cm.	Few drops.
16·7 ,,	Few drops.	17·7 ,,	Good shower.
17·7 ,,	Fair shower.	18·8 ,,	Dense coloured cloud.
18·8 ,,	Heavy shower.		

A comparison of C and D of the table shows that the glass-wool is instrumental in producing a very large number of nuclei, but it soon ceased to be effective, as after one day the effect produced for an expansion of 18·7 cm. was a very heavy shower. Its power was temporarily restored when air was drawn through the glass-wool after it had bubbled through water. The power of the glass-wool to produce nuclei was brought back and intensified in the following manner. When the glass-wool had ceased to produce nuclei and was strongly discoloured with iodine throughout its length, a small quantity of tap-water was sucked through it. The amount of water used was just sufficient to saturate half the wool. When air was drawn through, the wool became wet throughout its entire length and the air which got through contained an enormous number of nuclei. An expansion of 18·7 cm. produced a dense fog, but after one

day the effect diminished to a slightly tinted cloud. When the glass-wool was dried again by drawing dust-free air through it for a few hours, the effects obtained were again largely increased. These effects were very persistent, and experiments continued for more than a fortnight (during which dust-free air was drawn through the glass-wool for days) failed to remove the effect. By eliminating to a large extent the iodine, the effects were reduced but not got rid of, no doubt because of the difficulty of entirely getting rid of the iodine by simply drawing air through. The presence of fresh iodine quickly increased the effect again. The effect did not disappear when dry dust-free air was used in place of the ordinary air of the laboratory. After the glass-wool plug had been treated in this manner, it was left standing for a fortnight. The effect was found to have almost disappeared, but it reappeared when a few cubic centimetres of distilled water was drawn through, but the effect this time was not so persistent and disappeared almost entirely in the course of a few days. A similar amount of fresh distilled water brought back the effect, and this time it was very persistent. These experiments were made in Cape Town. Through the kindness of Professor Wilberforce I was able to repeat some of them at Liverpool University, using another apparatus and a different kind of glass-wool. The glass was obtained in the spun condition and was cut into lengths and the fibres separated just previous to the making of the plug used in the experiments, the result being somewhat heterogeneous glass-wool. A more important variation from the Cape Town experiments was in the water used to renew the effect in the glass-wool. This was of special purity, and was supplied to me through the courtesy of Mr. Powell of Liverpool University. The water was of the degree of purity required for accurate determinations of the resistivity of solutions. In this case also the effect was renewed in the glass-wool when a few cubic centimetres of this specially purified water was drawn through the plug.

Discussion of Results.

These experiments show that the purest water obtainable renews the effect in any kind of glass-wool. The conclusion drawn is that the effect does not depend in any way on the impurities which water contains. Other reasons supporting this conclusion are given further on. The fact that the effect can be renewed seems to prove that the effect is not caused by any impurity on the glass-wool. Owen and Pealing have shown that the effect obtained by the interaction of the

iodine and the Wilson's apparatus was renewed by rinsing the apparatus with distilled water, and the properties of the nuclei produced were the same, except possibly in size, as those produced by the glass-wool. Since the effect produced in the glass-wool is renewed by drawing distilled water over its surface, the conclusion seems irresistible that the nuclei produced in the two cases are due to the same chemical action.

The question arises, what is the nature of this chemical action? In the communication referred to above we gave a discussion of this. Three possible kinds of chemical action were considered :—

1. That the chemical action was one between the iodine and some impurity on the surface of the glass.

2. That the chemical action was a surface action between the glass and the iodine or one of its chemical compounds.

3. That it was a chemical action between iodine and water-vapour and oxygen caused by a catalytic action of the glass.

We considered that the weight of evidence entitled us to reject the impurity explanation in the case of the Wilson's apparatus alone, and this conclusion I now extend to the glass-wool. We considered that the second explanation was the correct one for the Wilson apparatus, and that the third explanation might explain the results when using glass-wool.

Ramsauer objects to this view and puts forward the following evidence in favour of the first explanation *.

He says :—" In explanation of the effects there described I should like to call attention to our experiments †, where we have shown that glass-wool and every glass surface that has not been strongly heated continuously gives off adsorbed minor constituents of the air, which on the production of ozone by ultra-violet light always lead to the formation of nuclei ; now, according to Mr. Owen himself, ozone is formed in his experiments. The regeneration of the effect on washing the walls with distilled water is explained by the fact that the water must contain dissolved small quantities of the vapours and gases mentioned before ‡ (for instance NH_3), and as it trickles down gives these up to the glass walls through adsorption. These observations led us to construct asbestos

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* Phil. Mag. May 1912.

† P. Lenard and C. Ramsauer, " Ueber die Wirkungen sehr kurzwelligen ultravioletten Lichtes auf Gase und über eine sehr reiche Quelle dieses Lichtes," *Heidelberger Akademie*. Five parts : I. Aug. 2, 1910 ; II. Nov. 5, 1910 ; III. Dec. 20, 1910 ; IV. June 9, 1911 ; V. Aug. 4, 1911.

‡ CO_2, NH_3, organic vapours, etc.

filters of combustion-glass, which could always be cleansed by being heated to redness, while glass-wool or cotton-wool filters, which are generally used finally to free a current of purified air from dust, have just the opposite effect, and charge the air again with all the impurities which have been previously removed, thus vitiating the results."

In reply to these objections, I would point out that his conclusions rest upon the assumptions that ozone is produced by the interaction of iodine and water, viz.

$$H_2O + I \longrightarrow HI + HIO,$$

$$HIO + O_2 \longrightarrow HI + O_3.$$

So far as I am aware no proof exists that this chemical action goes on under the conditions of our experiments. (Ramsauer's reference to our experiments establishing that fact is a mistake.)   What evidence there was, negatived that conclusion.   If such an action goes on, then the water should become acid, but it was found that it was of the same degree of acidity after several days' exposure to the iodine as it was before its introduction to the apparatus.   But Ramsauer's explanation seems to break down much more completely when we consider the reappearance of the effect on washing the apparatus.   Experiments showed that the introduction of water into the apparatus up to about 100 cc. in amount had no appreciable result on the effect so long as the surface of the glass was not rinsed in the process.   Hence, if Ramsauer's explanation is correct, the amount of water necessary to introduce sufficient impurity to bring back the effect must be of the order of many kilograms.   That is, the apparatus must be rinsed with several kilograms of water before the glass walls are saturated with the minor impurities he mentions, and the iodine effect would continue until all these impurities were exhausted.   It may be urged that only a small part of the impurity contained in that amount of water is absorbed by the glass.   It is very unlikely that this is the case with the water contained in the apparatus (of the amount of 200 grms. approximately).   Now in a case like this the effect is very much smaller on the second day after the introduction of the iodine, and by the fourth day has entirely disappeared.   That is, on Ramsauer's theory the impurity necessary to keep the effect going at an appreciable rate for two days is contained in an amount of water which cannot be more than 200 grams.   Now when we come to consider the case of the glass-wool, we find that when so

small an amount of water as 8 grams or less is used to clean the glass-wool, nuclei are produced which exceed very much in number the maximum effect obtained when using the glass walls of the apparatus (although it had, previous to the cleansing, produced practically no nuclei, no matter how much air was drawn through it), and this action continued for more than a fortnight. Hence in this case, if we adopt Ramsauer's theory, 8 grams of water would hold enough impurity to keep the effect in action at a somewhat accelerated rate for fourteen days. It is easy to see that we adopt a very low estimate when we say that 8 grams of water in the one case produces at least seven times the effect of 200 grams in the other.

When the glass-wool is freshly used and presumably saturated with impurities, the effect has practically disappeared in two days. To explain the continuance of the effect for a fortnight on a subsequent occasion, other circumstances being the same, we should have to assume that either all the impurity was not exhausted in the first case, or else we get a considerable supersaturation in the second. Both these explanations seem untenable. The experiments with the glass-wool show that the effect obtained does not depend upon the amount of water used, but on the amount and nature of glass surface exposed. This is particularly brought out in the experiments with the specially purified water. All the experiments support the third explanation that the nuclei are produced in a chemical action between iodine and oxygen and probably water-vapour aided by a catalytic property of glass. The increased action produced by the glass-wool is explained by its greater catalytic property. The disappearance of the effect is explained by the disappearance of the catalytic property, caused probably by the deposition of iodine or one of its products upon the glass surface. If this explanation is correct, then the action of the glass walls of the apparatus must be catalytic also.

The second explanation, that the action ceased because chemical equilibrium was established, is not essential and there are many objections to this theory. All the experimental facts are consonant with the third explanation, but I am unable definitely to state that it is the correct one.

XLV. *The Tracks of the α Particles in Sensitive Photographic Films.* *By* S. KINOSHITA, *Assistant Professor of Physics, and* H. IKEUTI, *Research Student, Imperial University, Tokyo* *.

[Plate VII.]

IN 1910 one of the writers † showed that each α particle produces a detectable effect on a photographic film, *i. e.* whenever an α particle strikes a grain of silver halide in the sensitive film, that grain is subsequently capable of development. It was also shown that this is the case throughout the whole range of the α particles. These conclusions were afterwards confirmed by the experiment of Reinganum ‡. On a microscopic examination of a photographic plate, to which the α rays had been tangentially projected, he observed that the path of each α particle appeared as a trail of silver grains. Reinganum drew attention to the fact that some of the trails showed the effect of scattering. Experiments on this subject were later made by Michl § and Mayer ‖ in more detail. Recently, Walmsley and Makower¶ succeeded in taking some microphotographs on which the deflected paths of the α particles were beautifully demonstrated. We have also been engaged in the study of the same problem and now allow ourselves to give a brief account of the results.

In investigating the photographic traces of the α rays it was considered effective to work with a possibly small source of the rays. For, if a point-like source be established and placed on a photographic plate, the expelled α particles will leave on it a set of radial traces, which can be followed with greater ease and certainty.

What we have utilized for the source of the α rays was a sewing-needle, carrying at its pointed end a minute quantity of the active deposit of radium. This could be easily prepared by lightly rubbing the point on a metal piece which had previously been exposed to a few millicuries of radium emanation. After the active needle had been in contact with a photographic plate for a short time, the plate was developed in the usual way, when a fine spot became visible to the

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* Communicated by Prof. H. Nagaoka.
† S. Kinoshita, Proc. Roy. Soc. A. lxxxiii. p. 432 (1910).
‡ Reinganum, *Phys. Zeits.* xii. p. 1076 (1911).
§ Michl, *Wien. Ber.* cxxi. 2 *a*, p. 1431 (1912).
‖ Mayer, *Ann. d. Phys.* xli. p. 931 (1913).
¶ Walmsley and Makower, Proc. Phys. Soc. xxvi. p. 261 (1914).

naked eye. As a matter of fact, it was not essential to keep the needle in contact with the plate throughout the time of exposure. A momentary touch seemed to be sufficient, if a proper interval of time was afterwards allowed to elapse before development, indicating that a part of the active deposit was detached from the needle and left behind on the plate at the point of contact. In some cases, a metal piece coated with the active deposit was, while being held above the plate, knocked with a finger, when similar results were obtained. In these cases, some dust particles adhering to the metal piece must have been set free by the shock and have settled down on the plate.

On examining the plate under a microscope, the said spot is seen to consist of a multitude of the radial trails of silver grains around a circular dark nucleus, to which reference will soon be made. A closer examination shows that these trails of grains are, in general, to be divided into two sets. Those constituting the first set emerge at the rim of the nucleus and end very nearly at the circumference of a circle drawn outside the nucleus and thus present themselves as a halo. The second set of the trails, on the other hand, spread out around the nucleus over a wide region with no sharply defined boundary. By focussing the microscope, it can be ascertained that the silver grains constituting the latter set of trails are all found in the uppermost layer of the sensitive film.

It was, however, not always the case that both of these sets are equally conspicuous. In some cases, one of them was particularly pronounced while the other was hardly visible.

The nucleus above mentioned is undoubtedly the cavity in the gelatin film produced by the point of the needle when it was brought into contact, and has nothing to do with the α particles. Its size is various in different photographs, depending on the circumstances under which the needle was held ; the greater the pressure applied to the needle, the larger the size of the nucleus. It may be added here that the pointed end of the needle had the shape of a truncated cone terminating in a flat section, which, as measured under a microscope, had a diameter of about ·01 mm. When the needle had been held with such a care that it hardly touched the plate, the photograph showed no dark nucleus. The same fact was often experienced when an active dust particle was the source of the α rays. Figs. 2 and 7 (Pl. VII.) are the examples.

In the photographs, in which a large number of trails

are radiating from a centre, each trail does not appear isolated from the others along the whole length, but, in the vicinity of the centre, comes very close to or overlaps the neighbouring ones.   This effect gives rise to another circular dark area in the middle, though it has no well-defined boundary.   The radius of the dark area varies of course as the number of the trails.   As this dark area covers the dark nucleus above spoken of, it sometimes makes the boundary of the latter indistinct.

The radius of the halo varies slightly in different plates from one another, but the length of each constituent radial trail or the difference of the radii of a halo and the circular nucleus inside it, is the same for all the haloes and equal to about ·054 mm. in the case of Ilford's Process Plates.   It is most probable that this represents the range of the α particles from radium C in the substance, as, in these cases, we used active deposit in which radium A had practically decayed away.   The silver grains constituting this set of trails are not restricted within the uppermost layer of the film, but found also in layers within some depth beneath the surface.   From these facts, it is evident that the halo is produced by a similar process as the pleochroic halo seen in the mineral such as biotite, and investigated in detail by Joly.   In the present case, however, a spherical halo cannot be expected, as the film on the plate employed was equivalent to only about 2 cm. of air in stopping the α rays, as calculated from its weight ·0030 gramme per square centimetre [*].   In order to show the haloes at different stages of formation, we have reproduced some of the microphotographs in figs. 1–6 (Pl. VII.).   These were taken with a microphotographic apparatus by Zeiss, the magnification being 380 diameters.   Fig. 1 shows a halo in which about 80 tracks are to be seen, this being of course the number of tracks on the plane focussed in reproducing and forming only a small fraction of the total.   The tracks which do not radiate from the centre are due to other sources lying outside the halo.   A fairly developed halo is shown in fig. 6, which, on our estimation, contains about 200 tracks.   The spots covering the greater part of the figure are due to dirt on the plate.   Figs. 2, 3, 4 and 5 are haloes at intermediate stages of formation.   On the plate containing the halo in fig. 2, there are, besides, several extended sources of radiation, whose effect is visible on one side of this figure.   We have counted the number of grains in each trail and found it to be about 16 on the average.

[*] Kinoshita, *l. c.* p. 437.

Attempts were also made to obtain a halo which is due to the α rays from radium A as well as radium C. For this purpose a metal piece was exposed to radium emanation for a few seconds, and the active deposit quickly detached from it was used as the source of the α rays. Closely examining the haloes thus obtained, it was found that among the trails of grains there are some which have a considerably shorter length than the others and seem to be those produced by the α rays from radium A. But we have not yet been able to get one clearly shown as a corona, as in the case of the pleochroic halo.

We have already drawn attention to the fact that the silver grains, which constitute the set of the trails spreading over a wide region, have their seats in the uppermost layer of the film. Fig. 7 is an example, of which the magnification is the same as that of the haloes. This fact suggests the view that these trails of grains are produced by the α particles projected tangentially to the surface of the film from the part of the active deposit just above the surface. At first sight, some of the trails seem to be much longer than those constituting the haloes. Careful inspection, however, shows that this is only apparent and that each of them consists of two or more elementary trails, having the average range of ·054, following one another.

So far, we have presumably treated the problem as the results of the α ray effect, and no account was taken for the β rays which are emitted as well from the active deposit of radium. It has long been known that the β rays possess the property of acting on a photographic plate ; but owing to difficulties involved in the experiment, very little is known about the effect of an individual β particle. In the experiment of Kinoshita already referred to, the photographic action of β rays was found to be about one-third or one-quarter of that of α rays in the case of a thinly coated Wratten's Ordinary Plate. In this calculation it was assumed that active deposit from radium emanation, in which radium A had already decayed away, emits about the same number of α and β particles. Since it is now known that the active deposit emits, under this circumstance, about twice as many β as α particles, the ratio of the photographic action of a β particle to that of an α particle reduces to only one-sixth or one-eighth. It therefore seemed likely that a silver halide grain bombarded by a β particle is not necessarily capable of development. If this be the case, the track of a β particle would not be so closely filled up with the developed grains as in the case of an α particle. It

is quite possible that the developed grains follow one another with too wide intervals to present themselves as a track of a β particle, much more so when the liability of scattering of the rays is considered. It will be of interest to recall that, in the well-known experiment of C. T. R. Wilson, a considerable difference was observed between the α and β particles in forming a track in air. We are inclined to believe that the grains spreading out over a wide region in a far less definite manner are to be attributed to the β particles.

We shall next describe some experiments made in magnetic fields. A photographic plate was brought into contact with an active needle in the way already stated and quickly introduced between the poles of a powerful electromagnet, the plate being held perpendicular to the lines of magnetic force. When the plate seemed to have been exposed to a sufficient number of α particles, it was withdrawn and developed immediately. Working, however, in a field up to nearly ten thousand gauss, no indication of curving of the track was observed. Taking the velocity of the α particle as 2×10^9 cm. per sec., it can be shown that the particle should, in a field of 10,000 gauss, describe a path for which the radius of curvature is as great as 40 centimetres. Such a slight curvature would not easily be recognized, as the length of the path under examination is so minute, that it is only about ·054 mm.

Evidences have already been given by the previously cited investigators that many of the α particles suffer sudden deflexions on the passage through the emulsion film. On the microphotographs taken by Walmsley and Makower, this effect is seen exceedingly well. This phenomenon can be observed on our photographs too. Fig. 8 (Pl. VII.) is the microphotograph of a plate in which the α particles passed from left to right, the magnification being in this case 1,210 diameters. It can be seen that, while one of the α particles passed straight on, another suffered a sudden deflexion of about 15° after traversing some distance nearly parallel to the former. It may be remarked, that we have examined a great number of sets of the radial tracks of the α particles, but so far we have not been able to find any which can be said with certainty to have suffered the deflexion of an angle so large as 90°. The number of the tracks showing such a large deflexion seems to be one in several thousands at most.

In the halo with a thrust-mark inside, such as that in fig. 5, many of the radial tracks are seen to be curved in

a wave-form. This is possibly due to ununiform contraction of the gelatin film in the vicinity of the pierced point as it dried from the wet state in development process, and therefore cannot be interpreted as the effect of deflexions.

In a series of experiments, a photographic plate was placed in contact with a flat piece of glass coated with the active deposit of radium in the usual way, and thus exposed to the α rays coming out of the source of large area. On examining the plate under a microscope, a considerable proportion of the tracks seemed to have suffered large deflexions. Moreover, in these cases, it seemed that there were as many tracks showing large deflexions as those showing small deflexions. Consequently, further investigations will be necessary to settle the question, whether these tracks are actually due to single α particles or to two particles passing through the film in different directions.

In conclusion, we wish to thank Professor Nagaoka for his kind interest in this experiment. We must also thank Professor Tawara of the Metallurgical Department for his kindness in allowing us to use the microphotographic apparatus.

September, 1914.

XLVI. *On the Electron Theory of Metallic Conduction.*—II. *By* G. H. Livens [*].

T HE modern theory of electrical conduction in metals is based on the assumption that every metallic body contains a large number of electrons moving about quite freely in the space between the atoms. Both electrons and atoms are presumed to be perfectly elastic spheres[†], the latter being of such comparatively large mass that their energy and motion may be neglected. In the absence of an external field it is presumed that the electrons are moving with the velocities assigned to them by Maxwell's law, according to which there are

$$\mathrm{N}\sqrt{\frac{q^3}{\pi^3}}\,e^{-qr^2}d\xi\,d\eta\,d\zeta$$

electrons per unit volume with the components of velocity

between (ξ, η, ζ) and $(\xi+d\xi, \eta+d\eta, \zeta+d\zeta)$. In this expression N represents the total number of free electrons per unit volume and

$$r^2 = \xi^2 + \eta^2 + \zeta^2 ;$$

q is a constant connected with the mean value $u_m{}^2$ of the square of the resultant velocity of each electron by the relation

$$q = \frac{3}{2u_m{}^2}.$$

If a uniform field of strength E is brought into play parallel to the x-axis of coordinates, this velocity distribution will be immediately altered. Each electron will acquire momentum parallel to the same axis at a rate eE (e being the charge on it), but this gain will be held in check by a perpetual transfer of momentum between each electron and all the molecules by which it is influenced at any instant. Exactly how this transfer takes place we do not yet know, but some such interaction between the electrons and the atoms during the encounters over and above the ordinary quasi-elastic reactions seems to be necessary in order to ensure the maintenance of a steady state. We can, however, make good progress in the theory without assuming very much about such interactions, and two alternative methods of attack have been suggested.

Lorentz assumes that a new steady state of motion of the electrons is attained, once the steady current is well established, and by statistical considerations regarding the effect of collisions and the electric force on the distribution he finds that in such a steady state the new velocity distribution may be approximately expressed by saying that

$$\mathrm{N}\sqrt{\frac{q^3}{\pi^3}}\Big(1+\frac{2qe\mathrm{E}l_m\xi}{mr}\Big)e^{-qr^2}d\xi\,d\eta\,d\zeta \;*$$

is the number of electrons per unit volume with velocity components between (ξ, η, ζ) and $(\xi+d\xi, \eta+d\eta, \zeta+d\zeta)$: in this expression m represents the mass of the typical electron and l_m the mean free path. This of course means that there are at any instant more electrons on the average moving

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* It is here assumed that there are no thermal effects in action. Lorentz's theory is, however, sufficiently general to include these actions, but they modify the distribution of velocities here quoted. The present mode of analysis is easily extended to such cases.

with any definite velocity in the positive direction of the x-axis than in the negative direction. By calculating the transfer of electricity resulting from such a distribution Lorentz is led to his well-known formula for the electrical conductivity.

On the other hand Drude, Riecke, Thomson, Wilson, and others take rather a different view of the matter. According to these authors the whole effect imparted by the electric force on the electron during its free-path motion is obliterated by the collision at the end of the path, so that each free path is started with the velocity the electron would have had throughout it, in the absence of any field of force : the distribution of the initial velocities in the paths is thus that specified by Maxwell's law given above.

The object of the present paper is to show that these two views, which at first sight appear to be rather contradictory, are in reality probably the same, or at least that they are consistent with one another. Although on *a priori* grounds one would certainly prefer to accept Lorentz's view of the situation, yet detailed consideration of the matter rather inclines one towards the perhaps less general but certainly more direct methods of Drude and Thomson. I will not, however, presume to dogmatize on the relative merits of the two forms of the theory.

We shall consider the problem of conduction from the point of view that the initial velocities at the beginning of the free paths are distributed according to Maxwell's law, each impact removing all effects imparted to the electron by the electric field previous to it. The peculiarity of this assumption is that it does not give the law of distribution of the velocities of the electrons at any particular instant, but rather the law of distribution of the initial velocities at the beginning of the free paths being pursued at that instant, the instant of beginning the free paths being, however, different for the different electrons. The actual law for the distribution of the velocities at any particular instant can, however, easily be deduced and in the following manner.

Consider the electrons and their motion at any instant in their free paths : the number of the electrons per unit volume which started their current free paths with their velocity components between (ξ, η, ζ) and $(\xi+d\xi, \eta+d\eta, \zeta+d\zeta)$ is given by Maxwell's law, and is thus equal to

$$dN = N\sqrt{\frac{q^3}{\pi^3}}e^{-qr^2}d\xi d\eta d\zeta \quad . \quad . \quad . \quad . \quad \text{(i.)}$$

Of these $d\mathrm{N}$ electrons the number

$$d\mathrm{N} = \frac{d\mathrm{N}}{\tau_m} e^{-\frac{\tau}{\tau_m}} d\tau * \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \text{(ii)}$$

have been in motion since their last impact previous to the instant t for a time which is between τ and $\tau + d\tau$. In this expression τ_m represents the mean value of the various values of τ for this particular group of electrons †.

Now the velocity components of any one of the group of electrons specified by (ii.) are at the instant t given by

$$(\xi', \eta', \zeta') \equiv (\xi + \frac{e\mathrm{E}\tau}{m}, \eta, \zeta).$$

Thus all of them will have these components within the limits (ξ', η', ζ'), $(\xi' + d\xi', \eta' + d\eta', \zeta' + d\zeta')$, and we may put

$$d\xi' = d\xi, \quad d\eta' = d\eta, \quad d\zeta' = d\zeta.$$

If, therefore, we interpret (ii.) in terms of $\xi', \eta', \zeta', \tau$ we may conclude that there is the number

$$\delta\mathrm{N}' = \delta\mathrm{N} = \frac{\mathrm{N}}{\tau_m} \sqrt{\frac{q^3}{\pi^3}} e^{-q\left[\left(\xi' - \frac{e\mathrm{E}\tau}{m}\right)^2 + \eta'^2 + \zeta'^2\right] - \frac{\tau}{\tau_m}} d\xi' d\eta' d\zeta' d\tau$$

of the electrons per unit volume whose velocity components at the instant t lie between (ξ', η', ζ') and $(\xi' + d\xi', \eta' + d\eta', \zeta' + d\zeta')$ and for which the time τ lies between τ and $\tau + d\tau$.

If we use

$$r'^2 = \xi'^2 + \eta'^2 + \zeta'^2$$

and if, as is usually the case, we may neglect terms involving E^2, this expression reduces to

$$\frac{\mathrm{N}}{\tau_m} \sqrt{\frac{q^3}{\pi^3}} e^{-qr'^2 - \left(1 - \frac{2e\mathrm{E}\tau_m \xi'}{m}\right)\frac{\tau}{\tau_m}} d\xi' d\eta' d\zeta' d\tau.$$

Thus on integration over all the values of τ we find that the total number of electrons with velocity components in the specified limits at the instant t is given by

$$\mathrm{N}\sqrt{\frac{q^3}{\pi^3}} \cdot \frac{e^{-qr'^2}}{1 - \frac{2e\mathrm{E}\tau_m \xi'}{m}} d\xi' d\eta' d\zeta',$$

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* *Vide* Lorentz, ' The Theory of Electrons,' p. 308.

† This value of τ_m also appears to be the mean duration of a free path in the more general case.

which is practically the same as

$$N\sqrt{\frac{q^3}{\pi^3}}\,e^{-qr'^2}\Big(1+\frac{2e E \tau_m \xi'}{m}\Big)d\xi'd\eta'd\zeta'.$$

Now, noticing that τ_m only occurs in the small correction term, we may replace it by the approximate value

$$\tau_m = \frac{l_m}{r'},$$

so that we deduce the law of distribution of velocities at any instant in the steady state and under the action of the uniform electric force E in the form

$$dN' = N\sqrt{\frac{q^3}{\pi^3}}\,e^{-qr'^2}\Big(1+\frac{2e E l_m \xi'}{mr'}\Big)d\xi'd\eta'd\zeta',$$

which is precisely Lorentz's result *.

It thus appears that under the assumptions made by Drude and Thomson the average steady distribution of velocities is precisely that derived by Lorentz. I think also it is clear that the argument may be reversed, or, in other words, that the steady distribution calculated on general grounds by Lorentz necessarily implies that the distribution of initial velocities is that specified by Maxwell's law. The two modes of formulation of the theory are consequently ultimately identical, although they are apparently very different in form.

The mode of deduction of Lorentz's formula here suggested can be extended so as to apply to the more general problem with varying fields. As an example we may, for instance, calculate the average distribution of velocities at any instant when the perfectly irregular motion of the electrons is modified by the application of a simple periodic electric force, say

$$E = E_0 \cos p(t+t')$$

where t is used for the time t at which we evaluate the distribution, and t' is an auxiliary time variable which is measured from the instant t as origin. Under these circumstances we find, with the same notation as before,

$$\xi' = \xi + \frac{e E_0}{pm}\{\sin pt - \sin p(t-\tau)\}$$

$$= \xi + \frac{2e E_0}{pm}\cos p\Big(t-\frac{\tau}{2}\Big)\sin p\frac{\tau}{2},$$

while
$$\eta' = \eta, \qquad \zeta' = \zeta.$$

* In this expression l_m is legitimately interpreted as the length of the mean free path.

Thus the number of electrons with velocity components between the limits (ξ', η', ζ') and $(\xi' + d\xi', \eta' + d\eta', \zeta' + d\zeta')$, and for which the time τ lies between τ and $\tau + d\tau$, is

$$\delta N' = \frac{N}{\tau_m} \sqrt{\frac{q^3}{\pi^3}} e^x d\xi' d\eta' d\zeta' d\tau,$$

where x is used for the argument of the exponential function, and is equal to

$$x = -q\left[\left(\xi' - \frac{2eE_0}{pm}\cos p\left(t - \frac{\tau}{2}\right)\sin\frac{p\tau}{2}\right)^2 + \eta'^2 + \zeta'^2\right] - \frac{\tau}{\tau_m},$$

which is practically the same as

$$x = -q\left[r'^2 - \frac{4eE_0\xi'}{pm}\cos p\left(t - \frac{\tau}{2}\right)\sin\frac{p\tau}{2}\right] - \frac{\tau}{\tau_m}.$$

Thus to the same order of approximation * we find that

$$\delta N' = \frac{N}{\tau_m}\sqrt{\frac{q^3}{\pi^3}} e^{-qr'^2}\left[1 + \frac{4eE_0\xi'}{pm}\cos p\left(t - \frac{\tau}{2}\right)\sin\frac{p\tau}{2}\right] e^{-\frac{\tau}{\tau_m}} d\xi' d\eta' d\zeta' d\tau.$$

Integrating with respect to τ from 0 to ∞ we find the total number of the electrons with their velocity components between $(\xi'\eta'\zeta')$ and $(\xi' + d\xi', \eta' + d\eta', \zeta' + d\zeta')$ is

$$dN' = N\sqrt{\frac{q^3}{\pi^3}} e^{-qr'^2}\left[1 + \frac{2eE_0\xi'}{pm}\left\{\frac{p\tau_m\cos pt + p^2\tau_m^2\sin pt}{1 + \sqrt{p^2\tau_m^2}}\right\}\right] d\xi' d\eta' d\zeta';$$

or again using

$$\tau_m = \frac{l_m}{r'}$$

we get

$$dN' = N\sqrt{\frac{q^3}{\pi^3}} e^{-qr'^2}\left[1 + \frac{2el_mE_0\xi'}{mr'}\left\{\frac{\cos pt + \frac{pl_m}{r'}\sin pt}{1 + \frac{p^2l_m^2}{r^2}}\right\}\right] d\xi' d\eta' d\zeta'.$$

Following Lorentz we find that under these circumstances the current of electricity at the instant t is

$$J = \frac{2Ne^2l_mE_0}{m}\sqrt{\frac{q^3}{\pi^3}}\iiint\frac{\xi'^2}{r'} e^{-qr'^2}\frac{\cos pt + \frac{pl_m}{r'}\sin pt}{1 + \frac{p^2l_m^2}{r^2}} d\xi' d\eta' d\zeta';$$

* *i. e.*, neglecting all terms involving squares or higher powers of E.

or again using

$$\xi'^2 = \tfrac{1}{3} r'^2 \quad \text{and} \quad d\xi' d\eta' d\zeta' = 4\pi r'^2 dr'$$

so that the integral reduces to a single integral in r' from 0 to ∞, we get

$$J = \frac{4\pi N e^2 l_m}{3m} \sqrt{\frac{q^3}{\pi^3}} \, E_0 \int_0^\infty \frac{2 r'^3 e^{-qr'^2}}{1 + \dfrac{p^2 l_m^2}{r'^2}} \left(\cos pt + \frac{p l_m}{r'} \sin pt \right) dr'.$$

On using $v = q r'^2$ we find

$$J = \frac{4 N e^2 l_m}{3m} \sqrt{\frac{q}{\pi}} \, E_0 \int_0^\infty \frac{v e^{-v}}{1 + \dfrac{p^2 l_m^2 q}{v}} \left(\cos pt + \frac{p l_m \sqrt{q}}{\sqrt{v}} \sin pt \right) dv$$

or

$$J = 2 \sqrt{\frac{2}{3\pi}} \cdot \frac{N e^2 l_m}{m u_m} \cdot E_0 (A \cos pt + B \sin pt),$$

wherein

$$A = \int_0^\infty \frac{v e^{-v} dv}{1 + \dfrac{p^2 l_m^2 q}{v}}, \qquad B = p l_m \sqrt{q} \int_0^\infty \frac{\sqrt{v} e^{-v} dv}{1 + \dfrac{p^2 l_m^2 q}{v}}.$$

If we use

$$\epsilon = \tan^{-1} \frac{B}{A}$$

we find that, again,

$$J = 2 \sqrt{\frac{2}{3\pi}} \frac{N e^2 l_m A}{m u_m} E_0 \cos (pt - \epsilon) \sec \epsilon.$$

The conductivity in such cases is defined usually by the average rate of dissipation of heat, which in the present case is the average value of

$$EJ = 2 \sqrt{\frac{2}{3\pi}} \frac{N e^2 l_m A}{m u_m} E_0^2 \cos pt \cos (pt - \epsilon) \sec \epsilon,$$

which is simply

$$\sqrt{\frac{2}{3\pi}} \frac{N e^2 l_m A}{m u_m} E_0^2,$$

whereas in terms of the conductivity it is known to be $\frac{1}{2}\sigma E_0^2$; so that

$$\sigma = 2\sqrt{\frac{2}{3\pi}}\frac{Ne^2l_m A}{mu_m}$$

$$= 2\sqrt{\frac{2}{3\pi}}\frac{Ne^2l_m}{mu_m}\int_0^\cdot \frac{ve^{-v}dv}{1+\dfrac{p^2l_m^2q_,}{v}}$$

which is the result obtained on the more direct method suggested by Thomson. For very long waves, it reduces, as it should, to Lorentz's original formula.

A full discussion of the actual bearing of these results on the electron theory of the optical properties of metals will be reserved for a future communication which is in course of preparation. The main point of the present paper seemed worthy of special and separate attention in the more general theory rather than in the restricted branch of it which is concerned with the optical properties only.

The University, Sheffield.
   Nov. 4th, 1914.

XLVII. *Notices respecting New Books.*

The Electrical Conductivity and Ionization Constants of Organic Compounds. By HEYWARD SCUDDER. Constable & Co., 1914. 12s. nett.

THIS is a bibliography, extending to 563 pages, of the periodical literature from 1889 to 1910, inclusive, including all important work before 1889 and corrected to the beginning of 1913, and gives numerical data for the ionization constants at all temperatures at which they have been measured and some numerical data of the electrical conductivity. The compilation thus deals with all the important work on the ionization constants and the electrical conductivity of organic compounds from the commencement up to the year 1910, at which date the Tables Annuelles International de Constants et Données Numériques begin. The book constitutes in its somewhat limited field a useful work of reference to those engaged in the subject. But unless it should prove in the future of value as a starting point in the comprehensive reexamination of the whole question from a theoretical standpoint, it may be doubted whether such a great expenditure of time and labour as the work has entailed has been profitably undertaken.
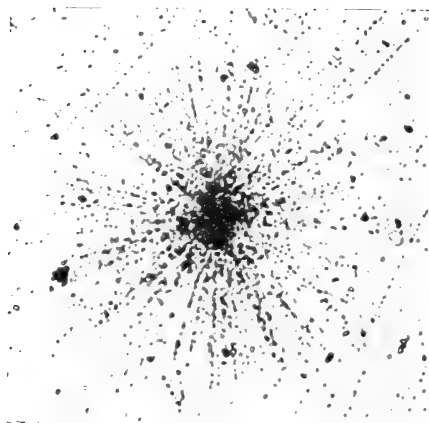
FIG. 1.
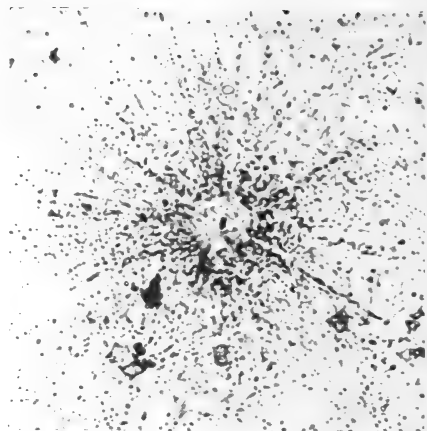
FIG. 2.
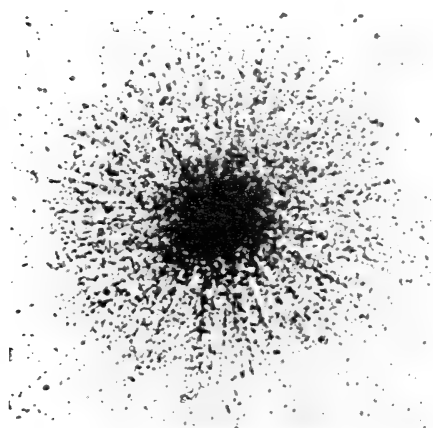
FIG. 3.
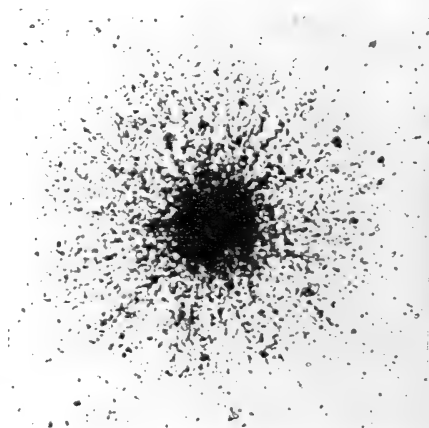
FIG. 4.
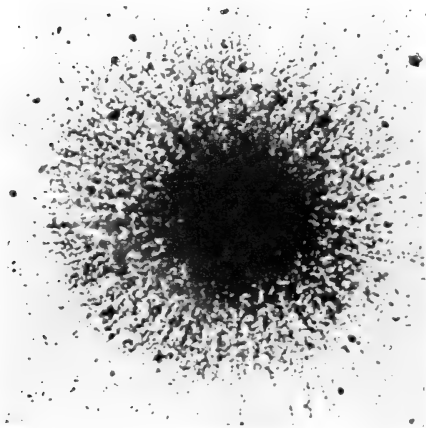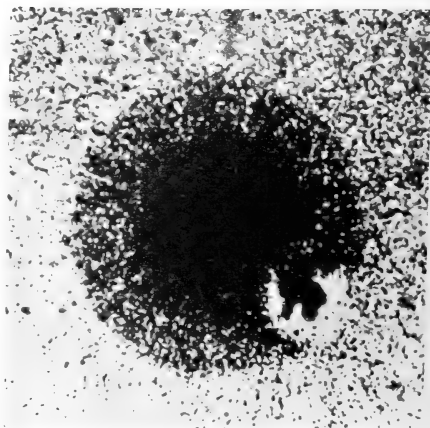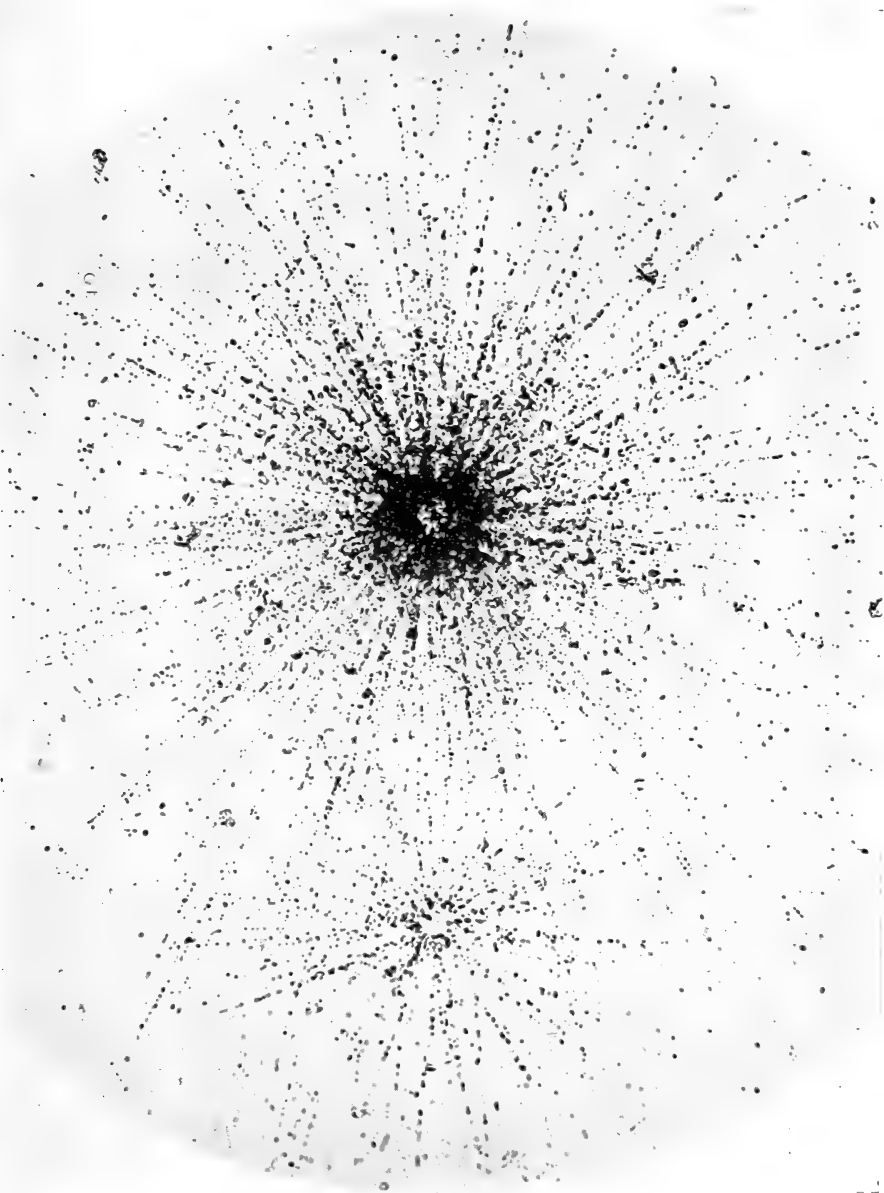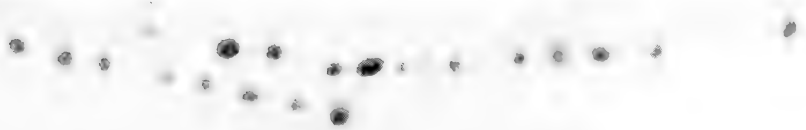
FIG. 5.

FIG. 6.

Fig. 7.

Fig. 8.
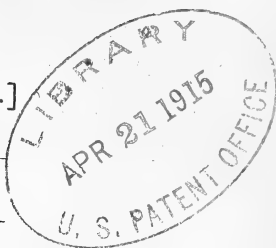
XLVIII. *Æolian Tones.*
By Lord Rayleigh, *O.M., F.R.S.*[*]

IN what has long been known as the Æolian Harp, a stretched string, such as a pianoforte wire or a violin string, is caused to vibrate in one of its possible modes by the impact of wind; and it was usually supposed that the action was analogous to that of a violin bow, so that the vibrations were executed in the plane containing the direction of the wind. A closer examination showed, however, that this opinion was erroneous and that in fact the vibrations are transverse to the wind[†]. It is not essential to the production of sound that the string should take part in the vibration, and the general phenomenon, exemplified in the whistling of wind among trees, has been investigated by Strouhal[‡] under the name of *Reibungstöne.*

In Strouhal's experiments a vertical wire or rod attached to a suitable frame was caused to revolve with uniform velocity about a parallel axis. The pitch of the æolian tone generated by the relative motion of the wire and of the air was found to be independent of the length and of the tension of the wire, but to vary with the diameter (D) and with the speed (V) of the motion. Within certain limits the relation

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[*] Communicated by the Author.

[†] Phil. Mag. vol. vii. p. 149 (1879); Scientific Papers, vol. i. p. 413.

[‡] Wied. *Ann.* vol. v. p. 216 (1878).

between the frequency of vibration (N) and these data was expressible by

$$N = \cdot 185 \, V/D, \quad . \quad . \quad . \quad . \quad (1)^*$$

the centimetre and the second being units.

When the speed is such that the æolian tone coincides with one of the proper tones of the wire, supported so as to be capable of free independent vibration, the sound is greatly reinforced, and with this advantage Strouhal found it possible to extend the range of his observations. Under the more extreme conditions then practicable the observed pitch deviated considerably from the value given by (1). He further showed that with a given diameter and a given speed a rise of temperature was attended by a fall in pitch.

If, as appears probable, the compressibility of the fluid may be left out of account, we may regard N as a function of the relative velocity V, D, and ν the kinematic coefficient of viscosity. In this case N is necessarily of the form

$$N = V/D \, . \, f(\nu/VD), \quad . \quad . \quad . \quad . \quad (2)$$

where f represents an arbitrary function; and there is dynamical similarity, if $\nu \propto VD$. In observations upon air at one temperature ν is constant; and if D vary inversely as V, ND/V should be constant, a result fairly in harmony with the observations of Strouhal. Again, if the temperature rises, ν increases, and in order to accord with observation, we must suppose that the function f diminishes with increasing argument.

"An examination of the actual values in Strouhal's experiments shows that ν/VD was always small; and we are thus led to represent f by a few terms of MacLaurin's series. If we take

$$f(x) = a + bx + cx^2,$$

we get

$$N = a \frac{V}{D} + b \frac{\nu}{D^2} + c \frac{\nu^2}{VD^3}. \quad . \quad . \quad . \quad (3)$$

" If the third term in (3) may be neglected, the relation between N and V is linear. This law was formulated by Strouhal, and his diagrams show that the coefficient b is negative, as is also required to express the observed effect of a rise of temperature. Further,

$$D \frac{dN}{dV} = a - \frac{c\nu^2}{V^2 D^2}, \quad . \quad . \quad . \quad . \quad (4)$$

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* In (1) V is the velocity of the wire relatively to the walls of the laboratory.

so that $D . dN/dV$ is very nearly constant, a result also given by Strouhal on the basis of his measurements.

"On the whole it would appear that the phenomena are satisfactorily represented by (2) or (3), but a dynamical theory has yet to be given. It would be of interest to extend the experiments to liquids."*

Before the above paragraphs were written I had commenced a systematic deduction of the form of f from Strouhal's observations by plotting ND/V against VD. Lately I have returned to the subject, and I find that nearly all his results are fairly well represented by two terms of (3). In c.g.s. measure

$$\frac{ND}{V} = \cdot 195\left(1 - \frac{3\cdot 02}{VD}\right). \quad . \quad . \quad . \quad . \quad (5)$$

Although the agreement is fairly good, there are signs that a change of wire introduces greater discrepancies than a change in V—a circumstance which may possibly be attributed to alterations in the character of the surface. The simple form (2) assumes that the wires are smooth, or else that the roughnesses are in proportion to D, so as to secure geometrical similarity.

The completion of (5) from the theoretical point of view requires the introduction of ν. The temperature for the experiments in which ν would enter most was about 20° C., and for this temperature

$$\nu = \frac{\mu}{\rho} = \frac{1806 \times 10^{-7}}{\cdot 00120} = \cdot 1505 \text{ c.g.s.}$$

The generalized form of (5) is accordingly

$$\frac{ND}{V} = \cdot 195\left(1 - \frac{20\cdot 1\,\nu}{VD}\right), \quad . \quad . \quad . \quad (6)$$

applicable now to any fluid when the appropriate value of ν is introduced. For water at 15° C., $\nu = \cdot 0115$, much *less* than for air.

Strouhal's observations have recently been discussed by Krüger and Lauth†, who appear not to be acquainted with my theory. Although they do not introduce viscosity, they recognize that there is probably some cause for the observed deviations from the simplest formula (1), other than the complication arising from the circulation of the air set in

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* 'Theory of Sound,' 2nd ed. vol. ii. § 372 (1896).
† "Theorie der Hiebtöne," *Ann. d. Physik*, vol. xliv. p. 801 (1914).

motion by the revolving parts of the apparatus. Undoubtedly this circulation marks a weak place in the method, and it is one not easy to deal with. On this account the numerical quantities in (6) may probably require some correction in order to express the true formula when V denotes the velocity of the wire through otherwise undisturbed fluid.

We may find confirmation of the view that viscosity enters into the question, much as in (6), from some observations of Strouhal on the effect of *temperature.* Changes in ν will tell most when VD is small, and therefore I take Strouhal's table XX., where D = ·0179 cm. In this there appears

$$t_1 = 11°, \quad V_1 = 385, \quad N_1/V_1 = 6·70, \quad \nu_1,$$
$$t_2 = 31°, \quad V_2 = 381, \quad N_2/V_2 = 6·48, \quad \nu_2.$$

Introducing these into (6), we get

$$6·70 - 6·48 = \frac{·195}{D}\left(1 - \frac{20·1\,\nu_1}{V_1 D}\right) - \frac{·195}{D}\left(1 - \frac{20·1\,\nu_2}{V_2 D}\right),$$

or with sufficient approximation

$$\nu_2 - \nu_1 = \frac{·52\,D^2 V}{·195 \times 20·1} = ·016 \text{ c.g.s.}$$

We may now compare this with the known values of ν for the temperatures in question. We have

$$\mu_{31} = 1853 \times 10^{-7}, \quad \rho_{31} = ·001161,$$
$$\mu_{11} = 1765 \times 10^{-7}, \quad \rho_{11} = ·001243;$$

so that

$$\nu_2 = ·1596, \qquad \nu_1 = ·1420,$$

and

$$\nu_2 - \nu_1 = ·018.$$

The difference in the values of ν at the two temperatures thus accounts in (6) for the change of frequency both in sign and in order of magnitude.

As regards dynamical explanation it was evident all along that the origin of vibration was connected with the instability of the vortex sheets which tend to form on the two sides of the obstacle, and that, at any rate when a wire is maintained in transverse vibration, the phenomenon must be unsymmetrical. The alternate formation in water of detached vortices on the two sides is clearly described by H. Bénard[*].

* *C. R.* t. 147, p. 839 (1908).

" Pour une vitesse suffisante, au-dessous de laquelle il n'y a pas de tourbillons (cette vitesse limite croît avec la viscosité et decroît quand l'épaisseur transversale des obstacles augmente), *les tourbillons produits périodiquement se detachent alternativement à droite et à gauche du remous d'arrière qui suit le solide; ils gagnent presque immédiatement leur emplacement définitif, de sorte qu'à l'arrière de l'obstacle se forme une double rangée alternée d'entonnoirs stationnaires, ceux de droite dextrogyres, ceux de gauche lévogyres, séparés par des intervalles égaux.*"

The symmetrical and unsymmetrical processions of vortices were also figured by Mallock[*] from direct observation.

In a remarkable theoretical investigation[†] Kármán has examined the question of the stability of such processions. The fluid is supposed to be incompressible, to be devoid of viscosity, and to move in two dimensions. The vortices are concentrated in points and are disposed at equal intervals (l) along two parallel lines distant h. Numerically the vortices are all equal, but those on different lines have opposite signs.

Apart from stability, steady motion is possible in two arrangements (a) and (b), fig. 1, of which (a) is symmetrical.

Fig. 1.
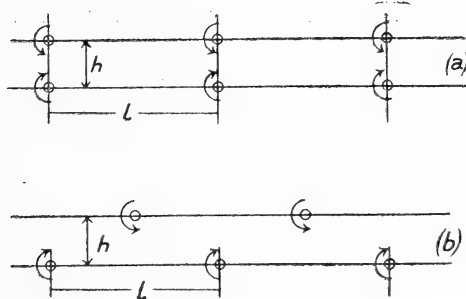
Kármán shows that (a) is always unstable, whatever may be the ratio of h to l; and further that (b) is usually unstable also. The single exception occurs when $\cosh (\pi h/l) = \sqrt{2}$, or $h/l = 0 \cdot 283$. With this ratio of h/l, (b) is stable for every kind of displacement except one, for which there is neutrality.

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[*] Proc. Roy. Soc. vol. lxxxiv. A. p. 490 (1910).
[†] *Göttingen Nachrichten*, 1912, Heft 5, S. 547; Kármán and Rubach, *Physik. Zeitschrift*, 1912, p. 49. I have verified the more important results.

The only procession which can possess a practical permanence is thus defined.

The corresponding motion is expressed by the complex potential (ϕ potential, ψ stream-function)

$$\phi + i\psi = \frac{i\zeta}{2\pi}\log\frac{\sin\{\pi(z_0 - z)/l\}}{\sin\{\pi(z_0 + z)/l\}}, \quad \cdots \quad (7)$$

in which ζ denotes the strength of a vortex, $z = x + iy$, $z_0 = \frac{1}{4}l + ih$. The x-axis is drawn midway between the two lines of vortices and the y-axis halves the distance between neighbouring vortices with opposite rotation. Kármán gives a drawing of the stream-lines thus defined.

The constant velocity of the processions is given by

$$u = \frac{\zeta}{2l}\tanh\frac{\pi h}{l} = \frac{\zeta}{l\sqrt{8}} \cdots \cdots (8)$$

This velocity is relative to the fluid at a distance.

The observers who have experimented upon water seem all to have used obstacles not susceptible of vibration. For many years I have had it in mind to repeat the æolian harp effect with water[*], but only recently have brought the matter to a test. The water was contained in a basin, about 36 cm. in diameter, which stood upon a sort of turn-table. The upper part, however, was not properly a table, but was formed of two horizontal beams crossing one another at right angles, so that the whole apparatus resembled rather a turn-*stile*, with four spokes. It had been intended to drive from a small water-engine, but ultimately it was found that all that was needed could more conveniently be done by hand after a little practice. A metronome beat approximate half seconds, and the spokes (which projected beyond the basin) were pushed gently by one or both hands until the rotation was uniform with passage of one or two spokes in correspondence with an assigned number of beats. It was necessary to allow several minutes in order to make sure that the water had attained its ultimate velocity. The axis of rotation was indicated by a pointer affixed to a small

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[*] From an old note-book. "Bath, Jan. 1884. I find in the baths here that if the spread fingers be drawn pretty quickly through the water (palm foremost was best), they are thrown into transverse vibration and strike one another. This seems like æolian string..... The blade of a flesh-brush about $1\frac{1}{2}$ inch broad seemed to vibrate transversely in its own plane when moved through water broadways forward. It is pretty certain that with proper apparatus these vibrations might be developed and observed."

stand resting on the bottom of the basin and rising slightly above the level of the water.

The pendulum (fig. 2), of which the lower part was immersed, was supported on two points (A, B) so that the

Fig. 2.
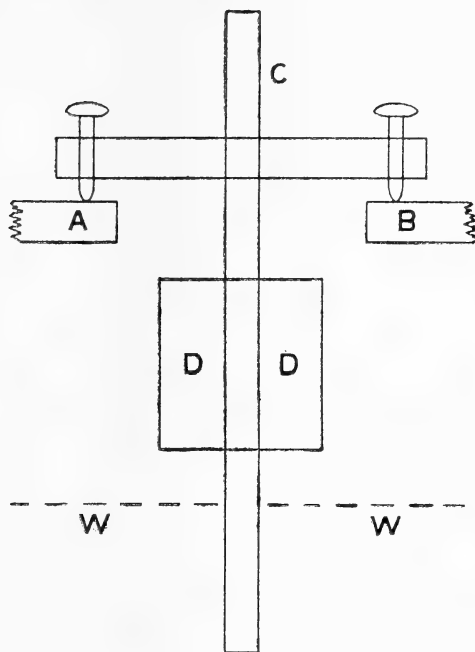
possible vibrations were limited to one vertical plane. In the usual arrangement the vibrations of the rod would be radial, *i. e.* transverse to the motion of the water, but it was easy to turn the pendulum round when it was desired to test whether a circumferential vibration could be maintained. The rod C itself was of brass tube $8\frac{1}{2}$ mm. in diameter, and to it was clamped a hollow cylinder of lead D. The time of complete vibration (τ) was about half a second. When it was desired to change the diameter of the immersed part, the rod C was drawn up higher and prolonged below by an additional piece—a change which did not much affect the period τ. In all cases the length of the part immersed was about 6 cm.

Preliminary observations showed that in no case were vibrations generated when the pendulum was so mounted that the motion of the rod would be circumferential, viz. in

the direction of the stream, agreeably to what had been found for the æolian harp. In what follows the vibrations, if any, are radial, that is transverse to the stream.

In conducting a set of observations it was found convenient to begin with the highest speed, passing after a sufficient time to the next lower, and so on, with the minimum of intermission. I will take an example relating to the main rod, whose diameter (D) is $8\frac{1}{2}$ mm., $\tau = 60/106$ sec., beats of metronome 62 in 30 sec. The speed is recorded by the number of beats corresponding to the passage of *two* spokes, and the vibration of the pendulum (after the lapse of a sufficient time) is described as small, fair, good, and so on. Thus on Dec. 21, 1914:

2 spokes to 4 beats gave fair vibration,
. . . . 5 . . . . good . . . .
. . . . 6 . . . . . rather more . . . .
. . . . 7 . . . . good . . . .
. . . . 8 . . . . fair . . . .

from which we may conclude that the maximum effect corresponds to 6 beats, or to a time (T) of revolution of the turn-table equal to $2 \times 6 \times 30/62$ sec. The distance (r) of the rod from the axis of rotation was 116 mm., and the speed of the water, supposed to move with the basin, is $2\pi r/\text{T}$. The result of the observations may intelligibly be expressed by the ratio of the distance travelled by the water during one complete vibration of the pendulum to the diameter of the latter, viz.

$$\frac{\tau \cdot 2\pi r/\text{T}}{\text{D}} = \frac{2\pi \times 116 \times 62}{8 \cdot 5 \times 6 \times 106} = 8 \cdot 36.$$

Concordant numbers were obtained on other occasions.

In the above calculation the speed of the water is taken as if it were rigidly connected with the basin, and must be an over estimate. When the pendulum is away, the water may be observed to move as a solid body after the rotation has been continued for two or three minutes. For this purpose the otherwise clean surface may be lightly dusted over with sulphur. But when the pendulum is immersed, the rotation is evidently hindered, and that not merely in the neighbourhood of the pendulum itself. The difficulty thence arising has already been referred to in connexion with Strouhal's experiments and it cannot easily be met in its entirety. It may be mitigated by increasing r, or by diminishing D. The latter remedy is easily applied up to a

certain point, and I have experimented with rods 5 mm. and $3\frac{1}{2}$ mm. in diameter. With a 2 mm. rod no vibration could be observed. The final results were thus tabulated :—

| Diameter ... | 8·5 mm. | 5·0 mm. | 3·5 mm. |
| Ratio ...... | 8·35 | 7·5 | 7·8 |

from which it would appear that the disturbance is not very serious. The difference between the ratios for the 5·0 mm. and 3·5 mm. rods is hardly outside the limits of error ; and the prospect of reducing the ratio much below 7 seemed remote.

The instinct of an experimenter is to try to get rid of a disturbance, even though only partially ; but it is often equally instructive to increase it. The observations of Dec. 21 were made with this object in view ; besides those already given they included others in which the disturbance due to the vibrating pendulum was augmented by the addition of a similar rod ($8\frac{1}{2}$ mm.) immersed to the same depth and situated symmetrically on the same diameter of the basin. The anomalous effect would thus be doubled. The record was as follows :—

> 2 spokes to 3 beats gave little or no vibration,
> .... 4 .... fair ......
> .... 5 .... large ......
> .... 6 .... less ......
> .... 7 .... little or no ......

As the result of this and another day's similar observations it was concluded that the 5 beats with additional obstruction corresponded with 6 beats without it. An approximate correction for the disturbance due to improper action of the pendulum may thus be arrived at by decreasing the calculated ratio in the proportion of 6 : 5 ; thus

$$\tfrac{5}{6}(8\cdot35)=7\cdot0$$

is the ratio to be expected in a uniform stream. It would seem that this cannot be far from the mark, as representing the travel at a distance from the pendulum in an otherwise uniform stream during the time of one complete vibration of the latter. Since the correction for the other diameters will be decidedly less, the above number may be considered to apply to all three diameters experimented on.

In order to compare with results obtained from air, we must know the value of ν/VD. For water at 15° C. $\nu=\mu=\cdot0115$ c.g.s. ; and for the 8·5 mm. pendulum $\nu/\text{VD}=\cdot0011$. Thus from (6) it appears that ND/V should

have nearly the full value, say ·190. The reciprocal of this, or 5·3, should agree with the ratio found above as 7·0 ; and the discrepancy is larger than it should be.

An experiment to try whether a change of viscosity had appreciable influence may be briefly mentioned. Observations were made upon water heated to about 60° C. and at 12° C. No difference of behaviour was detected. At 60° C. $\mu = ·0049$, and at 12° C. $\mu = ·0124$.

I have described the simple pendulum apparatus in some detail, as apart from any question of measurements it demonstrates easily the general principle that the vibrations are transverse to the stream, and when in good action it exhibits very well the double row of vortices as witnessed by dimples upon the surface of the water.

The discrepancy found between the number from water (7·0) and that derived from Strouhal's experiments on air (5·3) raises the question whether the latter can be in error. So far as I know, Strouhal's work has not been repeated ; but the error most to be feared, that arising from the circulation of the air, acts in the wrong direction. In the hope of further light I have remounted my apparatus of 1879. The draught is obtained from a chimney. A structure of wood and paper is fitted to the fireplace, which may prevent all access of air to the chimney except through an elongated horizontal aperture in the front (vertical) wall. The length of the aperture is 26 inches (66 cm.), and the width 4 inches (10·2 cm.) ; and along its middle a gut string is stretched over bridges.

The draught is regulated mainly by the amount of fire. It is well to have a margin, as it is easy to shunt a part through an aperture at the top of the enclosure, which can be closed partially or almost wholly by a superposed card. An adjustment can sometimes be got by opening a door or window. A piece of paper thrown on the fire increases the draught considerably for about half a minute.

The string employed had a diameter of ·95 mm., and it could readily be made to vibrate (in 3 segments) in unison with a fork of pitch 256. The octave, not difficult to mistake, was verified by a resonator brought up close to the string. That the vibration is transverse to the wind is confirmed by the behaviour of the resonator, which goes out of action when held symmetrically. The sound, as heard in the open without assistance, was usually feeble, but became loud when the ear was held close to the wooden frame. The difficulty of the experiment is to determine the velocity of the wind, where it acts upon the string. I have attempted

to do this by a pendulum arrangement designed to determine the wind by its action upon an elongated piece of mirror (10·1 cm. × 1·6 cm.) held perpendicularly and just in front of the string. The pendulum is supported on two points— in this respect like the one used for the water experiments ; the mirror is above, and there is a counter-weight below. An arm projects horizontally forward on which a rider can be placed. In commencing observations the wind is cut off by a large card inserted across the aperture and just behind the string. The pendulum then assumes a sighted position, determined in the usual way by reflexion. When the wind operates the mirror is carried with it, but is brought back to the sighted position by use of a rider of mass equal to ·485 gm.

Observations have been taken on several occasions, but it will suffice to record one set whose result is about equal to the average. The (horizontal) distance of the rider from the axis of rotation was 62 mm., and the vertical distance of the centre line of the mirror from the same axis is 77 mm. The force of the wind upon the mirror was thus $62 \times ·485 \div 77$ gms. weight. The mean pressure P is

$$\frac{62 \times ·485 \times 981}{77 \times 16·2} = 23·7 \frac{\text{dynes}}{\text{cm.}^2}.$$

The formula connecting the velocity of the wind V with the pressure P may be written

$$P = C\rho V^2,$$

where ρ is the density; but there is some uncertainty as to the constancy of C. It appears that for large plates C = ·62, but for a plate 2 inches square Stanton found C = ·52. Taking the latter value [*], we have

$$V^2 = \frac{23·7}{·52\rho} = \frac{23·7}{·52 \times ·00123},$$

on introduction of the value of ρ appropriate to the circumstances of the experiment. Accordingly

$$V = 192 \text{ cm./sec.}$$

The frequency of vibration (τ^{-1}) was nearly enough 256 ; so that

$$\frac{V\tau}{D} = \frac{192}{256 \times ·095} = 7·9.$$

In comparing this with Strouhal, we must introduce the

* But I confess that I feel doubts as to the diminution of C with the linear dimension.

appropriate value of VD, that is 19, into (5). Thus

$$\frac{V}{ND} = \frac{V\tau}{D} = 6\cdot 1.$$

Whether judged from the experiments with water or from those just detailed upon air, this (Strouhal's) number would seem to be too low; but the uncertainty in the value of C above referred to precludes any very confident conclusion. It is highly desirable that Strouhal's number should be further checked by some method justifying complete confidence.

When a wire or string exposed to wind does not itself enter into vibration, the sound produced is uncertain and difficult to estimate. No doubt the wind is often different at different parts of the string, and even at the same part it may fluctuate rapidly. A remedy for the first named cause of unsteadiness is to listen through a tube, whose open end is brought pretty close to the obstacle. This method is specially advantageous if we take advantage of our know-ledge respecting the mode of action, by using a tube drawn out to a narrow bore (say 1 or 2 mm.) and placed so as to face the processions of vortices behind the wire. In con-nexion with the fire-place arrangement the drawn out glass tube is conveniently bent round through 180° and continued to the ear by a rubber prolongation. In the wake of the obstacle the sound is well heard, even at some distance (50 mm.) behind; but little or nothing reaches the ear when the aperture is in front or at the side, even though quite close up, unless the wire is itself vibrating, But the special arrangement for a draught, where the observer is on the high pressure side, is not necessary; in a few minutes any one may prepare a little apparatus competent to show the effect. Fig. 3 almost explains itself. A is the drawn out glass tube;

Fig. 3.
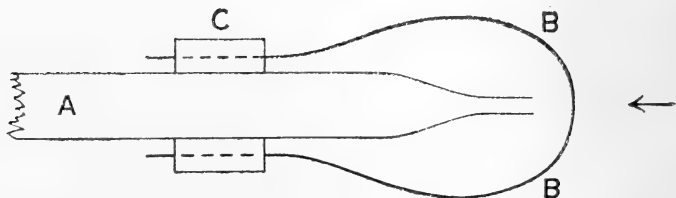
B the loop of iron or brass wire (say 1 mm. in diameter), attached to the tube with the aid of a cork C. The rubber prolongation is not shown. Held in the crack of a slightly opened door or window, the arrangement yields a sound which is often pure and fairly steady.

XLIX. *The Equations of Motion of a Viscous Fluid.* By
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of Applied Mathematics, University College, London* [*].

THE transformation of the equations of elasticity to curvi-
linear coordinates has been discussed by Lamé and
others, but the analogous equations for the motion of a
viscous fluid do not appear to have attracted the same
attention. The first section of this paper deals with the
transformation of the equations of motion. The terms in
the equations which express the resultant force on an element
of fluid are *mutatis mutandis* identical with the corresponding
terms in the equations for an elastic solid, but they are given
in a form which I believe to be new, and which lends itself
more readily to applications to particular systems of co-
ordinates. The terms which express the accelerations of the
fluid are different owing to the different assumptions which
underlie the two theories. The second section is devoted
to a discussion of the components of stress in curvilinear
coordinates. The theory is illustrated by applications to
cylindrical and spherical polar coordinates. In the remaining
two sections we discuss the special cases of axial and plane
motion respectively.

§ 1. *Transformation of the Equation of Motion.*

If u, v, w, X, Y, Z, are the components of velocity and
body force respectively, p the mean pressure, ρ the density,
and μ the coefficient of viscosity, the equations of motion of
a viscous fluid are [†]

$$\rho \frac{\mathrm{D}u}{\mathrm{D}t} = \rho \mathrm{X} - \frac{\partial p}{\partial x} + \frac{1}{3}\mu \frac{\partial}{\partial x}\left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}\right) + \mu \nabla^2 u,$$

and two similar equations.

These three equations may be replaced by a single vector
equation. If **v** be the velocity and F the externally applied
force, then using the relation

$$\mathrm{curl.curl}\ \mathbf{v} = \mathrm{grad.\ div.}\ \mathbf{v} - \nabla^2 \mathbf{v}\ [\ddagger],$$

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[*] Communicated by Prof. Karl Pearson, F.R.S.
[†] Lamb, 'Hydrodynamics,' p. 538.
[‡] In the usual vector notation

$$\mathrm{curl.\ curl}\ \mathbf{v} = [\nabla[\nabla \cdot \mathbf{v}]]$$
$$= \nabla(\nabla\mathbf{v}) - \nabla^2\mathbf{v}$$
$$= \mathrm{grad.\ div.}\ \mathbf{v} - \nabla^2\mathbf{v}.$$

the vectorial equation of motion is

$$\rho \frac{D\mathbf{v}}{Dt} = \rho \mathbf{F} - \text{grad.}\, p + \frac{4}{3}\,\mu\, \text{grad. div.}\, \mathbf{v} - \mu\, \text{curl. curl}\, \mathbf{v}\,^{*}. \quad (1)$$

The transformations of *div.* and *curl* follow at once from the definition of these operators in terms of surface and line integrals respectively.

If α, β, γ are orthogonal curvilinear coordinates, and if

$$h_1{}^2 = \left(\frac{\partial \alpha}{\partial x}\right)^2 + \left(\frac{\partial \alpha}{\partial y}\right)^2 + \left(\frac{\partial \alpha}{\partial z}\right)^2,$$

while h_2, h_3 are defined by the same operation carried out upon β, γ respectively, so that elements of arc measured along the normals to the coordinate surfaces at any point are

$$\frac{\delta\alpha}{h_1},\; \frac{\delta\beta}{h_2},\; \frac{\delta\gamma}{h_3},$$

then †

$$\text{curl}\, \mathbf{v} = h_2 h_3 \left\{ \frac{\partial}{\partial \beta}\left(\frac{w}{h_3}\right) - \frac{\partial}{\partial \gamma}\left(\frac{v}{h_2}\right) \right\},$$

$$h_3 h_1 \left\{ \frac{\partial}{\partial \gamma}\left(\frac{u}{h_1}\right) - \frac{\partial}{\partial \alpha}\left(\frac{w}{h_3}\right) \right\},\; h_1 h_2 \left\{ \frac{\partial}{\partial \alpha}\left(\frac{v}{h_2}\right) - \frac{\partial}{\partial \beta}\left(\frac{u}{h_1}\right) \right\},\; (2)$$

$$\text{div.}\, \mathbf{v} = h_1 h_2 h_3 \left\{ \frac{\partial}{\partial \alpha}\left(\frac{u}{h_2 h_3}\right) + \frac{\partial}{\partial \beta}\left(\frac{v}{h_3 h_1}\right) + \frac{\partial}{\partial \gamma}\left(\frac{w}{h_1 h_2}\right), \quad . \quad . \quad . \quad (3)$$

where u, v, w are the components of $\mathbf{v}$ along the normals to the surfaces $\alpha, \beta, \gamma = const.$ respectively. In (3) put $\mathbf{v} = grad.\phi$, and we obtain

$$\nabla^2\phi = h_1 h_2 h_3 \left\{ \frac{\partial}{\partial \alpha}\left(\frac{h_1}{h_2 h_3}\frac{\partial\phi}{\partial \alpha}\right) + \frac{\partial}{\partial \beta}\left(\frac{h_2}{h_3 h_1}\frac{\partial\phi}{\partial \beta}\right) + \frac{\partial}{\partial \gamma}\left(\frac{h_3}{h_1 h_2}\frac{\partial\phi}{\partial \gamma}\right) \right\}. (4)$$

By a second application of the operations implied in (2) we have, denoting the direction of a component by a suffix,

$$\text{curl}_\alpha\, \text{curl}\, \mathbf{v} = h_2 h_3 \left[\frac{\partial}{\partial \beta}\left\{ \frac{h_1 h_2}{h_3}\left(\frac{\partial}{\partial \alpha}\left(\frac{v}{h_2}\right) - \frac{\partial}{\partial \beta}\left(\frac{u}{h_1}\right) \right) \right\} \right.$$

$$\left. - \frac{\partial}{\partial \gamma}\left\{ \frac{h_3 h_1}{h_2}\left(\frac{\partial}{\partial \gamma}\left(\frac{u}{h_1}\right) - \frac{\partial}{\partial \alpha}\left(\frac{w}{h_3}\right) \right) \right\} \right].$$

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* *Cf.* the corresponding elastic equation, Love, 'Theory of Elasticity,' p. 138.

† Love, p. 54.

This can be transformed into an expression which while it appears more complex, is in reality simpler in application, namely,

$$\text{curl}_a \, \text{curl } \mathbf{v} =$$

$$h_1 \frac{\partial}{\partial \alpha}(\text{div. } \mathbf{v}) - \nabla^2 u + \frac{u}{h_1} \nabla^2 h_1 - u \frac{\partial}{\partial \alpha}(\nabla^2 \alpha) - \frac{h_1 v}{h_2} \frac{\partial}{\partial \alpha}(\nabla^2 \beta) - \frac{h_1 w}{h_3} \frac{\partial}{\partial \alpha}(\nabla^2 \gamma)$$

$$+ 2h_2{}^2 \frac{\partial h_1}{\partial \beta} \frac{\partial}{\partial \alpha}\left(\frac{v}{h_2}\right) - 2h_1 h_2 \frac{\partial h_2}{\partial \alpha} \frac{\partial}{\partial \beta}\left(\frac{v}{h_2}\right) + 2h_3{}^2 \frac{\partial h_1}{\partial \gamma} \frac{\partial}{\partial \alpha}\left(\frac{w}{h_3}\right)$$

$$- 2h_1 h_3 \frac{\partial h_3}{\partial \alpha} \frac{\partial}{\partial \gamma}\left(\frac{w}{h_3}\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

This expression is simplified if it is possible to choose one or more of the functions α, β, γ so that they are solutions of $\nabla^2 = 0$, or in the language of Lamé, so that they are *thermometric parameters.*

It remains to find appropriate expressions for the components of $\dfrac{D\mathbf{v}}{Dt}$. In Cartesian coordinates

$$\frac{D}{Dt}(u, v, w) = \left(\frac{\partial}{\partial t} + u\frac{\partial}{\partial x} + v\frac{\partial}{\partial y} + w\frac{\partial}{\partial z}\right)(u, v, w),$$

and this may be written in vector form

$$\frac{D\mathbf{v}}{Dt} = \frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla)\mathbf{v}.$$

The component of this vector equation in the α direction is

$$\left(\frac{D\mathbf{v}}{Dt}\right)_\alpha = \left(\frac{\partial \mathbf{v}}{\partial t}\right)_\alpha + h_1 u \frac{\partial u}{\partial \alpha} + h_2 v \frac{\partial u}{\partial \beta} + h_3 w \frac{\partial u}{\partial \gamma} . \quad . \quad (6)$$

Let λ be any fixed direction in space whose direction cosines are l, m, n, then the component of $\mathbf{v}$ in this direction is

$$\mathbf{v}_\lambda = \frac{u}{h_1}\left(l\frac{\partial \alpha}{\partial x} + m\frac{\partial \alpha}{\partial y} + n\frac{\partial \alpha}{\partial z}\right) + \frac{v}{h_2}\left(l\frac{\partial \beta}{\partial x} + m\frac{\partial \beta}{\partial y} + n\frac{\partial \beta}{\partial z}\right)$$

$$+ \frac{w}{h_3}\left(l\frac{\partial \gamma}{\partial x} + m\frac{\partial \gamma}{\partial y} + n\frac{\partial \gamma}{\partial z}\right).$$

Then

$$\left(\frac{\partial \mathbf{v}}{\partial t}\right)_\lambda = \frac{\partial \mathbf{v}_\lambda}{\partial t}$$

$$= \frac{\dot{u}}{h_1}\left(l\frac{\partial \alpha}{\partial x} + m\frac{\partial \alpha}{\partial y} + n\frac{\partial \alpha}{\partial z}\right) + \frac{\dot{v}}{h_2}\left(l\frac{\partial \beta}{\partial x} + m\frac{\partial \beta}{\partial y} + n\frac{\partial \beta}{\partial z}\right)$$

$$+ \frac{\dot{w}}{h_3}\left(l\frac{\partial \gamma}{\partial x} + m\frac{\partial \gamma}{\partial y} + n\frac{\partial \gamma}{\partial z}\right)$$

$$+ \dot{\alpha}\left\{ \begin{array}{l} u\left\{ l\frac{\partial}{\partial \alpha}\left(\frac{1}{h_1}\frac{\partial \alpha}{\partial x}\right) + m\frac{\partial}{\partial \alpha}\left(\frac{1}{h_1}\frac{\partial \alpha}{\partial y}\right) + n\frac{\partial}{\partial \alpha}\left(\frac{1}{h_1}\frac{\partial \alpha}{\partial z}\right) \right\} \\ + v\left\{ l\frac{\partial}{\partial \alpha}\left(\frac{1}{h_2}\frac{\partial \beta}{\partial x}\right) + m\frac{\partial}{\partial \alpha}\left(\frac{1}{h_2}\frac{\partial \beta}{\partial y}\right) + n\frac{\partial}{\partial \alpha}\left(\frac{1}{h_2}\frac{\partial \beta}{\partial z}\right) \right\} \\ + w\left\{ l\frac{\partial}{\partial \alpha}\left(\frac{1}{h_3}\frac{\partial \gamma}{\partial x}\right) + m\frac{\partial}{\partial \alpha}\left(\frac{1}{h_3}\frac{\partial \gamma}{\partial y}\right) + n\frac{\partial}{\partial \alpha}\left(\frac{1}{h_3}\frac{\partial \gamma}{\partial z}\right) \right\} \end{array} \right\} \begin{array}{l} + \text{similar} \\ \text{terms in } \dot{\beta}, \dot{\gamma}. \end{array}$$

Remembering that $\dot{\alpha} = h_1 u$, $\dot{\beta} = h_2 v$, $\dot{\gamma} = h_3 w$, and using the nine relations of the type *

$$\frac{\partial}{\partial \alpha}\left(\frac{1}{h_1}\frac{\partial \alpha}{\partial x}\right) = -\frac{\partial \beta}{\partial x}\frac{\partial}{\partial \beta}\left(\frac{1}{h_1}\right) - \frac{\partial \gamma}{\partial x}\frac{\partial}{\partial \gamma}\left(\frac{1}{h_1}\right),$$

$$\frac{\partial}{\partial \alpha}\left(\frac{1}{h_2}\frac{\partial \beta}{\partial x}\right) = \frac{h_2}{h_1}\frac{\partial \alpha}{\partial x}\frac{\partial}{\partial \beta}\left(\frac{1}{h_1}\right), \quad \frac{\partial}{\partial \alpha}\left(\frac{1}{h_3}\frac{\partial \gamma}{\partial x}\right) = \frac{h_3}{h_1}\frac{\partial \alpha}{\partial x}\frac{\partial}{\partial \gamma}\left(\frac{1}{h_1}\right),$$

and finally taking for the direction λ the normal to the surface $\alpha = const.$, we obtain

$$\left(\frac{\partial \mathbf{v}}{\partial t}\right)_\alpha = \dot{u} + h_1 u\left\{ h_2\frac{\partial}{\partial \beta}\left(\frac{1}{h_1}\right)v + h_3\frac{\partial}{\partial \gamma}\left(\frac{1}{h_1}\right)w \right\}$$

$$- h_1 h_2\frac{\partial}{\partial \alpha}\left(\frac{1}{h_2}\right)v^2 - h_1 h_3\frac{\partial}{\partial \alpha}\left(\frac{1}{h_3}\right)w^2.$$

$$\cdot \quad \cdot \quad \cdot \quad (7)$$

We can now write down the transformed equations of motion.

Let ν be the kinematic viscosity so that $\nu = \mu/\rho$, and let

$$\frac{\mathfrak{D}}{\mathfrak{D}t} \equiv \frac{\partial}{\partial t} + h_1 u\frac{\partial}{\partial \alpha} + h_2 v\frac{\partial}{\partial \beta} + h_3 w\frac{\partial}{\partial \gamma}, \quad \cdot \quad \cdot \quad (8)$$

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* *Ibid.* Note on moving axes, p. 539 ; or Lamé, *Coordonnées Curvilignes*, p. 74.

then the α component of (1) becomes

$$\frac{\mathfrak{D}u}{\mathfrak{D}t} + h_1 u\left(h_2\frac{\partial}{\partial\beta}\left(\frac{1}{h_1}\right)v + h_3\frac{\partial}{\partial\gamma}\left(\frac{1}{h_1}\right)w\right) - h_1 h_2\frac{\partial}{\partial\alpha}\left(\frac{1}{h_2}\right)v^2 - h_1 h_3\frac{\partial}{\partial\alpha}\left(\frac{1}{h_3}\right)w^2$$

$$= F_\alpha - \frac{h_1}{\rho}\frac{\partial p}{\partial\alpha} + \nu\left[\frac{h_1}{3}\frac{\partial}{\partial\alpha}(\text{div. }\mathbf{v}) + \nabla^2 u - \frac{u}{h_1}\nabla^2 h_1\right.$$

$$+ u\frac{\partial}{\partial\alpha}(\nabla^2\alpha) + \frac{h_1 v}{h_2}\frac{\partial}{\partial\alpha}(\nabla^2\beta) + \frac{h_1 w}{h_3}\frac{\partial}{\partial\alpha}(\nabla^2\gamma)$$

$$- 2h_2{}^2\frac{\partial h_1}{\partial\beta}\frac{\partial}{\partial\alpha}\left(\frac{v}{h_2}\right) + 2h_1 h_2\frac{\partial h_2}{\partial\alpha}\frac{\partial}{\partial\beta}\left(\frac{v}{h_2}\right)$$

$$\left. - 2h_3{}^2\frac{\partial h_1}{\partial\gamma}\frac{\partial}{\partial\alpha}\left(\frac{w}{h_3}\right) + 2h_1 h_3\frac{\partial h_3}{\partial\alpha}\frac{\partial}{\partial\gamma}\left(\frac{w}{h_3}\right)\right]. \quad \cdots \quad (9)$$

The corresponding equations in v, w, can at once be written down from symmetry.

Application to cylindrical and polar coordinates.—If we take cylindrical coordinates ϖ, θ, z, we have

$$h_1 = h_3 = 1 \quad \text{and} \quad h_2 = \frac{1}{\varpi}.$$

Most of the terms in (9) vanish and we have [*]

$$\frac{\mathfrak{D}u}{\mathfrak{D}t} - \frac{v^2}{\varpi} = F_\varpi - \frac{1}{\rho}\frac{\partial h}{\partial\varpi} + \nu\left[\frac{1}{3}\frac{\partial}{\partial\varpi}(\text{div. }\mathbf{v}) + \nabla^2 u - \frac{u}{\varpi^2} - \frac{2}{\varpi^2}\frac{\partial v}{\partial\theta}\right]$$

$$\frac{\mathfrak{D}v}{\mathfrak{D}t} + \frac{uv}{\varpi} = F_\theta - \frac{1}{\rho\varpi}\frac{\partial p}{\partial\theta} + \nu\left[\frac{1}{3\varpi}\frac{\partial}{\partial\theta}(\text{div. }\mathbf{v}) + \nabla^2 v - \frac{v}{\varpi^2} + \frac{2}{\varpi^2}\frac{\partial u}{\partial\theta}\right]$$

$$\frac{\mathfrak{D}w}{\mathfrak{D}t} = F_z - \frac{1}{\rho}\frac{\partial p}{\partial z} + \nu\left[\frac{1}{3}\frac{\partial}{\partial z}(\text{div. }\mathbf{v}) + \nabla^2 w\right].$$

From (3)

$$\text{div. }\mathbf{v} = \frac{1}{\varpi}\frac{\partial}{\partial\varpi}(\varpi u) + \frac{1}{\varpi}\frac{\partial v}{\partial\theta} + \frac{\partial w}{\partial z}$$

and is zero if the fluid is incompressible, while from (8)

$$\frac{\mathfrak{D}}{\mathfrak{D}t} = \frac{\partial}{\partial t} + u\frac{\partial}{\partial\varpi} + \frac{v}{\varpi}\frac{\partial}{\partial\theta} + w\frac{\partial}{\partial z}.$$

If r, θ, ϕ are spherical polar coordinates,

$$h_1 = 1, \quad h_2 = \frac{1}{r}, \quad h_3 = \frac{1}{r\sin\theta}.$$

[*] *Cf.* Basset, 'Hydrodynamics,' vol. ii. p. 244, where the equations are given for an incompressible fluid.

We have

$$\text{div. } \mathbf{v} = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2 u) + \frac{1}{r\sin\theta}\frac{\partial}{\partial\theta}(v\sin\theta) + \frac{1}{r\sin\theta}\frac{\partial w}{\partial\phi}$$

and

$$\frac{\mathfrak{D}}{t} = \frac{\partial}{\partial t} + u\frac{\partial}{\partial r} + \frac{v}{r}\frac{\partial}{\partial\theta} + \frac{w}{r\sin\theta}\frac{\partial}{\partial\phi},$$

and the equations of motion are *

$$\frac{\mathfrak{D}u}{\mathfrak{D}t} - \frac{v^2 + w^2}{r} = F_r - \frac{1}{\rho}\frac{\partial p}{\partial r} + \nu\left[\frac{1}{3}\frac{\partial}{\partial r}(\text{div. } \mathbf{v}) + \nabla^2 u\right.$$

$$\left. -\frac{2u}{r^2} - \frac{2\cot\theta}{r^2}v - \frac{2}{r^2}\frac{\partial v}{\partial\theta} - \frac{2}{r^2\sin\theta}\frac{\partial w}{\partial\phi}\right]$$

$$\frac{\mathfrak{D}v}{\mathfrak{D}t} + \frac{uv}{r} - \frac{w^2\cot\theta}{r} = F_\theta - \frac{1}{r\rho}\frac{\partial p}{\partial\theta} + \nu\left[\frac{1}{3r}\frac{\partial}{\partial\theta}(\text{div. } \mathbf{v}) + \nabla^2 v\right.$$

$$\left. -\frac{v}{r^2\sin^2\theta} - \frac{2\cos\theta}{r^2\sin^2\theta}\frac{\partial w}{\partial\phi} + \frac{2}{r^2}\frac{\partial u}{\partial\theta}\right]$$

$$\frac{\mathfrak{D}w}{\mathfrak{D}t} + \frac{uw}{r} + \frac{vw}{r}\cot\theta = F_\phi - \frac{1}{\rho r\sin\theta}\frac{\partial p}{\partial\phi} + \nu\left[\frac{1}{3r\sin\theta}\frac{\partial}{\partial\phi}(\text{div. } \mathbf{v})\right.$$

$$\left. + \nabla^2 w - \frac{w}{r^2\sin^2\theta} + \frac{2}{r^2\sin\theta}\frac{\partial u}{\partial\phi} + \frac{2\cos\theta}{r^2\sin^2\theta}\frac{\partial v}{\partial\phi}\right].$$

§ 2. *Transformation of the Stresses.*

If $\widehat{ns}$ denotes the component in the direction n of the stress across a surface whose normal is in the direction s and if the Cartesian components of velocity are u', v', w', we have

$$\widehat{xx} = -p + \lambda\delta + 2\mu\frac{\partial u'}{\partial x'}; \qquad \widehat{yz} = \mu\left[\frac{\partial w'}{\partial y} + \frac{\partial v'}{\partial z}\right];$$

where $\delta = \text{div. } \mathbf{v}$ and $\lambda = -\frac{2}{3}\mu$.

These are identical with the usual expressions for an elastic solid except for the term p, which indicates a pressure equal in all directions. The components of stress in an elastic solid were transformed to curvilinear coordinates by Lamé, and we can at once obtain the corresponding formulæ for a viscous fluid by inserting the uniform pressure p.

* *Cf.* Basset, p. 246, where a slight misprint occurs in the third equation.

Changing the notation to that which we have employed we have[*]

$$\widehat{\alpha\alpha} = -p + \lambda\delta + 2\mu h_1\left[\frac{\partial u}{\partial \alpha} + h_2\frac{\partial}{\partial \beta}\left(\frac{1}{h_1}\right)v + h_3\frac{\partial}{\partial \gamma}\left(\frac{1}{h_1}\right)w\right],$$

$$\widehat{\beta\gamma} = \mu\left[\frac{h_2}{h_3}\frac{\partial}{\partial \beta}(h_3 w) + \frac{h_3}{h_2}\frac{\partial}{\partial \gamma}(h_2 r)\right] = \widehat{\gamma\beta}, \quad . \quad . \quad . \quad . \tag{10}$$

and four similar equations.

For cylindrical coordinates we have, as before,

$$h_1 = h_3 = 1, \qquad h_2 = \frac{1}{\varpi},$$

and equations (10) give [†]

$$\widehat{\varpi\varpi} = -p + \lambda\delta + 2\mu\frac{\partial u}{\partial \varpi},$$

$$\widehat{\theta\theta} = -p + \lambda\delta + \frac{2\mu}{\varpi}\frac{\partial v}{\partial \theta} + \frac{2\mu}{\varpi}u,$$

$$\widehat{zz} = -p + \lambda\delta + 2\mu\frac{\partial w}{\partial z},$$

$$\widehat{\theta z} = \mu\left[\frac{1}{\varpi}\frac{\partial w}{\partial \theta} + \frac{\partial v}{\partial z}\right],$$

$$\widehat{z\varpi} = \mu\left[\frac{\partial u}{\partial z} + \frac{\partial w}{\partial r}\right],$$

$$\widehat{\varpi\theta} = \mu\left[\frac{\partial v}{\partial \varpi} - \frac{v}{\varpi} + \frac{1}{\varpi}\frac{\partial u}{\partial \theta}\right].$$

In the case of spherical polar coordinates r, θ, ϕ, we have

$$h_1 = 1, \qquad h_2 = \frac{1}{r}, \qquad h_3 = \frac{1}{r\sin\theta},$$

and equations (10) give [‡]

$$\widehat{rr} = -p + \lambda\delta + 2\mu\frac{\partial u}{\partial r},$$

$$\widehat{\theta\theta} = -p + \lambda\delta + 2\mu\left(\frac{1}{r}\frac{\partial v}{\partial \theta} + \frac{u}{r}\right),$$

$$\widehat{\phi\phi} = -p + \lambda\delta + 2\mu\left(\frac{u}{r} + \frac{v}{r}\cot\theta + \frac{1}{r\sin\theta}\frac{\partial w}{\partial \phi}\right),$$

$$\widehat{\theta\phi} = \mu\left(\frac{1}{r}\frac{\partial w}{\partial \theta} + \frac{1}{r\sin\theta}\frac{\partial v}{\partial \phi} - \frac{\cot\theta}{r}w\right),$$

$$\widehat{\phi r} = \mu\left(\frac{1}{r\sin\theta}\frac{\partial u}{\partial \phi} + \frac{\partial w}{\partial r} - \frac{w}{r}\right),$$

$$\widehat{r\theta} = \mu\left(\frac{\partial v}{\partial r} + \frac{1}{r}\frac{\partial u}{\partial \theta} - \frac{v}{r}\right).$$

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[*] Lamé, *Coordonnées Curvilignes*, p. 284.
[†] Lamé, *Leçons sur l'Elasticité*, p. 184.
[‡] *Elasticité*, p. 199. Some differences of sign are introduced by the fact that Lamé takes for the angle θ the latitude instead of the co-latitude.

Thus it will be seen that although the general formulæ are somewhat complex, yet when we apply them to particular sets of coordinates they become in many cases comparatively simple.

§ 3. *Axial Motion.*

The case in which we have symmetry of motion about an axis can be discussed by means of the equations in cylindrical coordinates. We will suppose the fluid to be incompressible and the external forces to be derivable from a potential V. Then writing

$$\chi = -V - \frac{p}{\rho},$$

and putting $\frac{\partial}{\partial \theta} = 0$ the equations in cylindrical coordinates become

$$\frac{\mathfrak{D}u}{\mathfrak{D}t} - \frac{v^2}{\varpi} = \frac{\partial \chi}{\partial \varpi} + \nu\left(\nabla^2 u - \frac{u}{\varpi^2}\right), \quad \dots \quad (11)$$

$$\frac{\mathfrak{D}v}{\mathfrak{D}t} + \frac{uv}{\varpi} = \nu\left(\nabla^2 v - \frac{v}{\varpi^2}\right). \quad \dots \quad (12)$$

$$\frac{\mathfrak{D}w}{\mathfrak{D}t} = \frac{\partial \chi}{\partial z} + \nu\nabla^2 w, \quad \dots \quad (13)$$

where

$$\frac{\mathfrak{D}}{\mathfrak{D}t} \equiv \frac{\partial}{\partial t} + u\frac{\partial}{\partial \varpi} + w\frac{\partial}{\partial z}.$$

The equation of continuity is

$$\frac{\partial}{\partial \varpi}(u\varpi) + \frac{\partial}{\partial z}(w\varpi) = 0,$$

and hence

$$u = -\frac{1}{\varpi}\frac{\partial \psi}{\partial z} ; \qquad w = \frac{1}{\varpi}\frac{\partial \psi}{\partial \varpi},$$

even if there is a velocity component perpendicular to the meridian plane.

Equation (12) becomes

$$\frac{\partial v}{\partial t} - \frac{1}{\varpi}\frac{\partial \psi}{\partial z}\frac{\partial v}{\partial \varpi} + \frac{1}{\varpi}\frac{\partial \psi}{\partial \varpi}\frac{\partial v}{\partial z} - \frac{1}{\varpi^2}\frac{\partial \psi}{\partial z}v = \nu\left(\nabla^2 v - \frac{v}{\varpi^2}\right).$$

Let

$$\varpi v = \Omega$$

and

$$\Phi \equiv \frac{\partial^2}{\partial \varpi^2} - \frac{1}{\varpi}\frac{\partial}{\partial \varpi} + \frac{\partial^2}{\partial z^2}$$

and we have

$$\frac{\partial(\psi, \Omega)}{\partial(\varpi, z)} = \varpi\left(v\Phi - \frac{\partial}{\partial t}\right)\Omega. \quad . \quad . \quad . \quad (14)$$

Eliminate χ between (11) and (13) and after some reduction we obtain

$$\frac{2}{\varpi}\left(\Omega\frac{\partial\Omega}{\partial z} + \frac{\partial\psi}{\partial z}\Phi(\psi)\right) + \frac{\partial(\psi, \Phi(\psi))}{\partial(\varpi, z)} = \varpi\left(v\Phi - \frac{\partial}{\partial t}\right)\Phi(\psi)$$

$$. \quad . \quad . \quad (15)$$

Then (14) and (15) are the equations for this type of motion.

One interesting result which flows from these equations is that the only possible motion, which consists of pure circulation about the axis without any accompanying motion in the meridian plane, is that generated by the rotation of two infinite coaxial circular cylinders about their common axis. Put $\psi = const.$ and (15) becomes

$$\frac{\partial\Omega}{\partial z} = 0,$$

and hence from (14), taking the case of steady motion,

$$\frac{d^2\Omega}{d\varpi^2} - \frac{1}{\varpi}\frac{d\Omega}{d\varpi} = 0,$$

the solution of which is

$$\Omega = A\varpi^2 + B,$$

or

$$v = A\varpi + \frac{B}{\varpi},$$

which is the solution referred to. Hence if any body of revolution other than a cylinder be rotated about its axis in a viscous fluid, the consequent motion of the fluid about the axis must in all cases be accompanied by a certain motion in the meridian plane. For the special case of a sphere this was pointed out by Stokes[*].

When the motion is entirely in the meridian plane, we have $\Omega = 0$. Equation (14) is identically satisfied and (15) becomes

$$\frac{\partial(\psi, \Phi(\psi))}{\partial(\varpi, z)} = \varpi\left(v\Phi - \frac{\partial}{\partial t} - \frac{2}{\varpi^2}\frac{\partial\psi}{\partial z}\right)\Phi(\psi),$$

[*] 'Mathematical and Physical Papers,' vol. i. p. 103.

which may be written

$$\left(\nu\Phi - \frac{\mathfrak{D}}{\mathfrak{D}t} - \frac{2}{\varpi^2}\frac{\partial\psi}{dz}\right)\Phi(\psi) = 0,$$

where $\dfrac{\mathfrak{D}}{\mathfrak{D}t}$ has the same meaning as before (p. 452).

These equations can readily be transformed to curvilinear coordinates should occasion arise since, apart from transformations already discussed, we require only the form of the operator Φ and this can be obtained from the identity

$$\Phi \equiv \nabla^2 - \frac{2}{\varpi}\frac{\partial}{\partial\varpi}.$$

§ 4. *Two-dimensional Motion.*

The equations for two-dimensional motion may be obtained as a particular case of the general equations, but they are more readily obtained from the Cartesian equations of motion. Using the same notation as before and taking the plane of xy as the plane of motion, we have

$$\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} = \frac{\partial\chi}{\partial x} + \nu\nabla^2 u,$$

$$\frac{\partial v}{\partial t} + u\frac{\partial v}{\partial x} + v\frac{\partial v}{\partial y} = \frac{\partial\chi}{\partial y} + \nu\nabla^2 v,$$

and

$$u = -\frac{\partial\psi}{\partial y}, \qquad v = \frac{\partial\psi}{\partial x},$$

where ψ is Earnshaw's current function.

Substituting these values for u, v and eliminating χ we have

$$\frac{\partial}{\partial t}(\nabla^2\psi) + \frac{\partial(\psi, \nabla^2\psi)}{\partial(x, y)} = \nu\nabla^4\psi.$$

Taking α, β, conjugate functions of x, y, as orthogonal curvilinear coordinates, we have from (4)

$$\nabla^2 \equiv \left\{\left(\frac{\partial\alpha}{\partial x}\right)^2 + \left(\frac{\partial\alpha}{\partial y}\right)^2\right\}\left\{\frac{\partial^2}{\partial\alpha^2} + \frac{\partial^2}{\partial\beta^2}\right\},$$

also

$$\frac{\partial(\psi, \nabla^2\psi)}{\partial(x, y)} = \frac{\partial(\psi, \nabla^2\psi)}{\partial(\alpha, \beta)} \cdot \frac{\partial(\alpha, \beta)}{\partial(x, y)}$$

$$= \left\{\left(\frac{\partial\alpha}{\partial x}\right)^2 + \left(\frac{\partial\alpha}{\partial y}\right)^2\right\}\frac{\partial(\psi, \nabla^2\psi)}{\partial(\alpha, \beta)}$$

so that the equation for ψ becomes

$$\frac{\partial}{\partial t}\left(\frac{\partial^2\psi}{\partial\alpha^2}+\frac{\partial^2\psi}{\partial\beta^2}\right)+\frac{\partial(\psi,\ \nabla^2\psi)}{\partial\ (\alpha,\ \beta)}=\nu\left(\frac{\partial^2}{\partial\alpha^2}+\frac{\partial^2}{\partial\beta^2}\right)\nabla^2\psi,$$

or

$$\frac{\partial(\psi,\ \nabla^2\psi)}{\partial(\alpha,\ \beta)}=\left(\frac{\partial^2}{\partial\alpha^2}+\frac{\partial^2}{\partial\beta^2}\right)\left(\nu\nabla^2\psi-\frac{\partial\psi}{\partial t}\right).$$

L. *The Two-Dimensional Steady Motion of a Viscous Fluid.* By G. B. JEFFERY, *M.A., B.Sc., Assistant in the Department of Applied Mathematics, University College, London*[*].

THE object of this paper is to search for some *exact* solutions of the equations of motion of a viscous fluid. Much has been accomplished by assuming that the motion is slow, and that the squares and products of the velocity components may therefore be neglected. It has indeed been held that this is the only useful proceeding, since the equations of motion are themselves formed on the assumption of a linear stress-strain relation, and this is probably only justifiable if the motion is sufficiently slow. On the other hand, there is very little evidence of the breakdown of the linear law in the case of fluids, and in any case it is only possible to test its validity by an investigation of solutions which do not require the motion to be slow. It is, therefore, of some importance to obtain some solutions which are free from this limitation. In the present paper we confine our attention to plane motion. Orthogonal curvilinear coordinates are employed, and we discuss the possibility of so choosing them that either the stream-lines or the lines of constant vorticity are identical with one family of the coordinate curves. The most important solutions obtained are those which correspond to (1) the motion round a canal in the form of a circular arc, (2) the motion between rotating circular cylinders with a given normal flow over the surfaces, as in a centrifugal pump, (3) the flow between two infinite planes inclined at any angle.

If u, v be the components of velocity, p the mean pressure, V the potential of the external forces, ν the kinematic viscosity, and ρ the density of the fluid, the equations of

motion in two dimensions are

$$\begin{aligned}
\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} &= -\frac{1}{\rho}\frac{\partial p}{\partial x} - \frac{\partial V}{\partial x} + \nu\nabla^2 u \\
\frac{\partial v}{\partial t} + u\frac{\partial v}{\partial x} + v\frac{\partial v}{\partial y} &= -\frac{1}{\rho}\frac{\partial p}{\partial y} - \frac{\partial V}{\partial y} + \nu\nabla^2 v
\end{aligned}\right\} \quad . \quad (1)$$

Eliminating the pressure from these equations we have

$$\frac{\partial}{\partial t}(\nabla^2\psi) + \frac{\partial(\psi, \nabla^2\psi)}{\partial(x, y)} = \nu\nabla^4\psi,$$

where

$$u = -\frac{\partial\psi}{\partial y}, \quad v = \frac{\partial\psi}{\partial x},$$

ψ being Earnshaw's current function.

Take a system of orthogonal curvilinear coordinates defined by conjugate functions α, β of x, y. The equation for ψ may then be written

$$\frac{\partial(\psi, \nabla^2\psi)}{\partial(\alpha, \beta)} = \left(\frac{\partial^2}{\partial\alpha^2} + \frac{\partial^2}{\partial\beta^2}\right)\left(\nu\nabla^2\psi - \frac{\partial\psi}{\partial t}\right),$$

or if the motion is steady

$$\frac{\partial(\psi, \nabla^2\psi)}{\partial(\alpha, \beta)} = \nu\left(\frac{\partial^2}{\partial\alpha^2} + \frac{\partial^2}{\partial\beta^2}\right)\nabla^2\psi. \quad . \quad . \quad . \quad (2)$$

§ 1. *Solutions for which the lines of constant vorticity are a possible set of equipotential lines.*

The coordinates can be so chosen that the curves $\alpha = const.$ are identical with any given set of equipotential lines in free space. Hence the characteristic property of this type of solution is that it is possible to choose the system of coordinates α, β so that $\nabla^2\psi$ is a function of α only, say

$$\nabla^2\psi = f(\alpha).$$

Substitute in (2) and we have

$$-\frac{\partial\psi}{\partial\beta} \cdot f'(\alpha) = \nu f''(\alpha),$$

or

$$\frac{\partial\psi}{\partial\beta} = -\nu\frac{d}{d\alpha}(\log f'(\alpha)).$$

Integrating with respect to β

$$\psi = -\nu\beta\frac{d}{d\alpha}(\log f'(\alpha)) + F(\alpha).$$

Hence

$$\nabla^2 \psi = \left\{ \left(\frac{\partial \alpha}{\partial x} \right)^2 + \left(\frac{\partial \beta}{\partial x} \right)^2 \right\} \left\{ -\nu\beta \frac{d^3}{d\alpha^3}(\log f'(\alpha)) + \mathrm{F}''(\alpha) \right\} = f(z).$$

Using a well-known property of conjugate functions this may be written

$$\left| \frac{d(x+iy)}{d(\alpha+i\beta)} \right|^2 = -\nu\beta \frac{1}{f(\alpha)} \frac{d^3}{d\alpha^3}(\log f'(\alpha)) + \frac{\mathrm{F}''(\alpha)}{f(\alpha)},$$

so that we have to determine a function of $\alpha + i\beta$ such that the square of its modulus is linear in β. Mr. G. N. Watson, to whom I submitted this problem, has supplied me with the complete solution. If

$$|\phi(\alpha + i\beta)|^2 = \mathrm{A}\beta + \mathrm{B},$$

where A, B are real functions of α, then

$$\phi(\alpha + i\beta) = \kappa\, e^{\lambda(\alpha + i\beta)},$$

where λ is real but κ may be complex. In this case

$$\mathrm{A} = 0, \qquad \mathrm{B} = |\kappa|^2\, e^{2\lambda\alpha}.$$

Applying this result to the problem in hand

$$\frac{d(x+iy)}{d(\alpha+i\beta)} = \kappa\, e^{\lambda(\alpha + i\beta)},$$

$$\frac{d^3}{d\alpha^3}(\log f'(\alpha)) = 0, \qquad \mathrm{F}''(\alpha) = |\kappa|^2 e^{2\lambda\alpha} f(\alpha).$$

Hence

$$f(\alpha) = \int e^{a\alpha^2 + b\alpha + c}\, d\alpha,$$

$$\mathrm{F}(\alpha) = |\kappa|^2 \iint (d\alpha)^2\, e^{2\lambda\alpha} \int e^{a\alpha^2 + b\alpha + c}\, d\alpha.$$

The constants κ, λ merely determine the scales of measurement in the different systems of coordinates, and we have only two distinct solutions (1) $\kappa = 1$, $\lambda = 0$, (2) $\kappa = 1$, $\lambda = 1$. The first case gives

$$\alpha + i\beta = x + iy,$$

and we have a solution in Cartesian coordinates

$$\psi = -\nu y(2ax + b) + \iiint e^{ax^2 + bx + c}\, (dx)^3.$$

If $a=0$ this gives

$$\psi = -bvy + \mathrm{A}\,e^{bx} + \mathrm{B}x^2 + \mathrm{C}x, \quad . \quad . \quad . \quad \text{(I.)}$$

while if a is not zero, a shift of origin gives

$$\psi = -2vaxy + \mathrm{A}\iiint e^{ax^2}\,(dx)^3. \quad . \quad . \quad \text{(II.)}$$

(I.) and (II.) are the only distinct solutions for which the lines of constant vorticity are a set of parallel straight lines. In the second case, when $\kappa=1$ and $\lambda=1$

$$\alpha + i\beta = \log\,(x+iy).$$

Hence, if $r,\ \theta$ be polar coordinates

$$\alpha = \log\,r, \qquad \beta = \theta,$$

and

$$\psi = -v\theta(2a\log r + b) + \int \frac{dr}{r}\int r\,dr\int e^{a(\log r)^2 + b(\log r) + c}\frac{dr}{r}.$$

This also leads to two distinct solutions according as a is or is not zero.

If $a=0$

$$\left.\begin{aligned} \psi &= -bv\theta + \mathrm{A}r^{b+2} + \mathrm{B}r^2 + \mathrm{C}\log r \quad (b\neq 0 \text{ or } -2)\\ &= 2v\theta + \mathrm{A}(\log r)^2 + \mathrm{B}r^2 + \mathrm{C}\log r \quad (b=-2), \end{aligned}\right\}\text{(III.)}$$

while if a is not zero, a change in the scale of r gives

$$\psi = -2va\theta\log r + \mathrm{A}\int \frac{dr}{r}\int r\,ar\int e^{a(\log r)^2}\frac{dr}{r}. \quad . \quad \text{(IV.)}$$

(III.), (IV.) are the only distinct solutions for which the lines of constant vorticity are a set of concentric circles. We have thus obtained all the solutions for which the lines of constant vorticity are the equipotential lines in free space of some possible distribution of matter.

§ 2. *Solutions for which the stream-lines are possible equipotential lines.*

The characteristic property of this type of solution is that it is possible to choose a set of curvilinear coordinates $\alpha,\ \beta$ so that $\psi = f(\alpha)$. It has not been found possible to solve this case with the generality of the previous section. Substituting in (2) we have

$$f'(\alpha)\frac{\partial}{\partial\beta}(\nabla^2\psi) = v\left(\frac{\partial^2}{\partial\alpha^2} + \frac{\partial^2}{\partial\beta^2}\right)\nabla^2\psi,$$

or writing

$$M = \left(\frac{\partial \alpha}{\partial x}\right)^2 + \left(\frac{\partial \beta}{\partial x}\right)^2,$$

we see that α, β, f are restricted by the condition that M must satisfy the equation

$$\nu f''(\alpha)\left(\frac{\partial^2 M}{\partial \alpha^2} + \frac{\partial^2 M}{\partial \beta^2}\right) + 2\nu f'''(\alpha)\frac{\partial M}{\partial \alpha} - f''(\alpha).f''(\alpha)\frac{\partial M}{\partial \beta}$$
$$+ \nu f''''(\alpha)M = 0. \quad . \quad . \quad . \quad (3)$$

This will be satisfied by any system α, β whatever, if $f'' = 0$, which corresponds to the otherwise obvious fact that any solution of $\nabla^2 \psi = 0$ is a solution of (2). Thus any irrotational motion is a possible motion of a viscous fluid.

Suppose

$$\alpha + i\beta = (x + iy)^n,$$

then

$$M = n^2 (\alpha^2 + \beta^2)^{\frac{n-1}{n}},$$

equation (3) gives

$$2\nu(n-1)(n-2)f''(\alpha) + 4\nu n(n-1)\alpha f'''(\alpha) - 2n(n-1)\beta f'(\alpha)f''(\alpha)$$
$$+ \nu n^2 f''''(\alpha)(\alpha^2 + \beta^2) = 0.$$

If $n = 1$, it is sufficient that $f''''(\alpha) = 0$, which leads to the well-known solution for the motion between infinite parallel planes :

$$\psi = Ax^3 + Bx^2 + Cx.$$

Otherwise, equating coefficients of powers of β separately to zero,

$$f''''(\alpha) = 0, \quad f'(\alpha)\,f''(\alpha) = 0, \quad f'''(\alpha) = 0.$$

Hence $f(\alpha)$ is a linear function of α, which corresponds to the case of irrotational motion. It appears, therefore, that for no value of n other than unity is there any new solution of this class.

Next consider polar coordinates r, θ. Equation (2) becomes

$$\frac{\partial(\psi, \nabla^2\psi)}{\partial(r, \theta)} = \nu r \nabla^4 \psi, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and

$$\nabla^2 = \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2},$$

First seek a solution of the form

$$\psi = f(r).$$

From (4)
$$\frac{d}{dr}\left(r \frac{d}{dr}\left(\frac{1}{r}\frac{d}{dr}\left(r \frac{d\psi}{dr}\right)\right)\right)=0,$$

and hence
$$\psi = Ar^2 \log r + Br^2 + C \log r. \quad . \quad . \quad . \quad (\text{V.})$$

Next seek a solution for which ψ is a function of θ only. Let
$$\psi = \Theta$$

then
$$\nabla^2\psi = \frac{1}{r^2}\Theta''$$

and
$$\nabla^4\psi = \frac{1}{r^4}(4\Theta'' + \Theta'''').$$

Substituting in (4)
$$2\Theta'\Theta'' = 4\nu\Theta'' + \nu\Theta''''.$$

Integrating
$$\Theta'^2 = 4\nu\Theta' + \nu\Theta''' + a,$$

and
$$\frac{\Theta'^3}{3} = 2\nu\Theta'^2 + \nu\frac{\Theta''^2}{2} + a\Theta' + b,$$

or
$$\theta = \sqrt{\frac{3\nu}{2}}\int \frac{d\Theta'}{\sqrt{\Theta'^3 - 6\nu\Theta'^2 - 3a\Theta' - 3b}}.$$

This may be written
$$\theta = \frac{\sqrt{6\nu}}{2}\int \frac{d\Theta'}{\sqrt{(\Theta'-\lambda)(\Theta'-\mu)(\Theta'-6\nu+\lambda+\mu)}},$$

where λ, μ are constants.
    Write
$$\Theta' = \lambda \sin^2\phi + \mu \cos^2\phi,$$

and the integral becomes
$$\left\{\frac{6\nu-\lambda-2\mu}{6\nu}\right\}^{\frac{1}{2}}(\theta-\theta_0) = \int_0^\phi \frac{d\phi}{\sqrt{1 - \dfrac{\lambda-\mu}{6\nu-\lambda-2\mu}\sin^2\phi}}.$$

Finally introduce new constants, k, m
$$k^2 = \frac{\lambda-\mu}{6\nu-\lambda-2\mu}, \quad m^2 = \frac{6\nu-\lambda-2\mu}{6\nu},$$

and we have
$$\frac{\partial\psi}{\partial\theta} = \Theta' = 2\nu(1-m^2-k^2m^2) + 6\nu k^2 m^2 sn^2\{m(\theta-\theta_0)\}\,(\text{VI.})$$

where k, m, θ_0 are arbitrary constants.

§ 3. *Solutions which are independent of the degree of viscosity.*

If we consider the motion of a fluid between two concentric circular cylinders rotating with given angular velocities, an increase in the viscosity of the fluid would necessitate an increase in the couples which maintain the rotation of the cylinders, but otherwise the motion would be unchanged. This will be true for any solution for which ψ is independent of ν, *i. e.* the two sides of the equation (2) vanish separately. Taking the equation in its Cartesian form we have

$$\frac{\partial(\psi, \nabla^2\psi)}{\partial(x, y)} = 0, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and

$$\nabla^4\psi = 0. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

It will be noted that equation (6) is the usual equation for the two-dimensional motion of a viscous fluid on the assumption that it is so slow that squares and products of the velocities may be neglected. For an exact solution equation (5) must also be satisfied, and hence

$$\nabla^2\psi = f(\psi),$$

that is the vorticity is constant along each stream-line. Substituting in (6),

$$f''(\psi)\left\{\left(\frac{\partial\psi}{\partial x}\right)^2 + \left(\frac{\partial\psi}{\partial y}\right)^2\right\} + f'(\psi)f(\psi) = 0.$$

Hence either (1) the resultant velocity is a function of ψ, and is therefore constant along each stream-line, or (2) $f''(\psi)$ and $f'(\psi)$ are zero. In the latter case

$$\nabla^2\psi = \text{const.} = 4a, \text{ say}$$

of which the general solution is

$$\psi = a(x^2 + y^2) + \chi,$$

where χ is any solution of $\nabla^2\chi = 0$. Hence any solid body rotation superposed upon any irrotational motion is a possible motion of a viscous fluid. The only other solutions of this class are those for which the velocity and the vorticity are constant along each stream-line.

§ 4. *Discussion of solutions obtained.*

Flow between two planes inclined at any angle.— We will first consider solution VI. We may without loss of generality

take $\theta_0 = 0$, so that

$$\frac{d\psi}{d\theta} = 2\nu(1 - m^2 - m^2k^2) + 6\nu k^2 m^2 sn^2(m\theta, k).$$
$$= 2\nu(1 + 2m^2 - m^2k^2) - 6\nu m^2 dn^2(m\theta, k).$$

The stream-lines are all straight lines passing through the origin. If u be the velocity of the fluid

$$u = -\frac{1}{r}\frac{d\psi}{d\theta}.$$

The constants m, k can be chosen so that the velocity is zero when $\theta = \alpha$, and hence, since u is an even function of θ, when $\theta = -\alpha$, while the values of ψ appropriate to these two stream-lines differ by a given amount. Thus we have a solution for the motion of a fluid between two fixed planes inclined at an angle 2α due to a line source of given strength along their line of intersection, or if we exclude the origin, for the flow along a canal with converging banks. If Q is the total flux of fluid outwards from the origin

$$Q = -4\nu\alpha(1 + 2m^2 - m^2k^2) + 12\nu m^2 \int_0^\alpha dn^2(m\theta, k)d\theta.$$

Now
$$\int_0^\zeta dn^2(z, k)dz = \mathrm{E}(\zeta, k)$$

where E denotes the elliptic integral of the second kind. Hence

$$Q = -4\nu\alpha(1 + 2m^2 - m^2k^2) + 12\nu m\mathrm{E}(m\alpha, k).$$

This relation, together with

$$3k^2 m^2 sn^2(m\alpha, k) + 1 - m^2 - m^2k^2 = 0,$$

is sufficient to determine m and k. (N.B.—α must be expressed in circular measure.)

If the angle between the planes is small, we may write $sn \cdot z = z$, and we have as an approximation when the planes are nearly parallel

$$\frac{d\psi}{d\theta} = 2\nu\{1 - m^2 - m^2k^2(1 - 3m^2\theta^2)\}.$$

If the angle between the planes is $2a$ we have

$$1 - m^2 - m^2k^2(1 - 3m^2\alpha^2) = 0,$$

or
$$k^2 = \frac{1 - m^2}{m^2(1 - 3m^2\alpha^2)},$$

and
$$\frac{d\psi}{d\theta} = \frac{6\nu m^2(1 - m^2)}{1 - 3m^2\alpha^2}(\theta^2 - \alpha^2).$$

We see that to this approximation the velocity across any cross section follows the same parabolic law as in the flow between two parallel planes.

Solutions I., II., and IV. lead to some interesting sets of stream-lines. They cannot, however, be realized physically, and they seem to be of little importance. We pass to the consideration of solution III.

A centrifugal pump.—We have

$$\psi = -b\nu\theta + Ar^{b+2} + Br^2 + C \log r,$$

and the components of velocity are given by

$$u = -\frac{1}{r}\frac{\partial\psi}{\partial\theta} = \frac{b\nu}{r}$$

$$v = \frac{\partial\psi}{\partial r} = A(b+2)r^{b+1} + 2Br + \frac{C}{r}.$$

From the equations of motion we can determine the mean pressure. If there are no external forces

$$p = -4b\rho\nu B\theta + \rho f'(r),$$

where $f'(r)$ can readily be determined if necessary. If we include the whole of the space round the origin, p must be single valued, and hence $B=0$. In this case the solution corresponds to the motion generated by the rotation of a perforated cylinder, which, as it rotates, either sucks in or ejects fluid uniformly over its surface. The fluid may either flow away to infinity, or it may be absorbed by a coaxial porous cylinder, which may be at rest or may be rotating with any angular velocity. The total flux of fluid will determine b, while the angular velocities of the cylinders will determine A and C. Such an arrangement will be in fact a centrifugal pump. When the fluid is viscous vanes are not absolutely necessary, although, of course, they may increase the efficiency of the machine. If there is no second cylinder so that the fluid extends to infinity, then we must have $A=0$ if the fluid is flowing outwards, for in that case $b>0$. Let the radius of the cylinder be a, and let it rotate with angular velocity Ω, and eject a volume Q of fluid in unit time; then

$$C = a^2\Omega, \qquad b = Q/2\pi\nu,$$

and we find without difficulty,

$$p = p_0 - \frac{1}{8\pi^2\rho r^2}(4\pi^2 a^4\Omega^2 + Q^2),$$

where p_0 is the pressure at infinity. Thus we have the

pressure head created by the pump when it rotates with a given velocity and discharges a given volume of fluid per unit time.

Flow under pressure along a circular canal.—Finally, we will consider solution V.

$$\psi = Ar^2 \log r + Br^2 + C \log r.$$

If u, v are the radial and transverse components of velocity

$$u = -\frac{1}{r}\frac{\partial \psi}{\partial \theta} = 0,$$

$$v = \frac{\partial \psi}{\partial r} = 2Ar \log r + (A + 2B)r + \frac{C}{r}.$$

If $A = 0$, this is the well-known solution for rotating concentric cylinders. Using the equations of motion in polar coordinates we can without difficulty find the value of the mean pressure p.

$$p = 4\nu\rho A\theta + \rho f(r),$$

where

$$f(r) = 2A (\log r)^2(Ar^2 + C) + 2 \log r(ABr^2 + AC + 2BC)$$
$$+ \frac{1}{2}(A^2 + 4B^2)r^2 - \frac{1}{2}\frac{C^2}{r^2}.$$

The constants B, C may be chosen so that the velocity is zero for any two values of r, and we have the solution for the flow of a viscous fluid round a canal bounded by two concentric circular arcs. The pressure will not be constant across a radial cross-section, but will vary in a way which is represented by $f(r)$. It will be noted, however, that $f(r)$ contains only the squares of the coefficients A, B, C, and is therefore of the order of the square of the velocity.

Suppose the canal is bounded by circular arcs of radii a, b, which subtend an angle α at their common centre, and let P be the pressure difference between corresponding points on the two bounding cross-sections. Then

$$P = 4\mu A\alpha,$$

where μ is the coefficient of viscosity and is therefore equal to $\nu\rho$. The condition that the velocity shall vanish when $r = a$, b gives the following equations to determine the constants B, C

$$A(r \log r^2 + r) + 2Br + \frac{C}{r} = 0, \quad (r = a, b),$$

from which we have

$$B = -\frac{A(a^2 \log a^2 - b^2 \log b^2 + a^2 - b^2)}{2(a^2 - b^2)}$$

$$C = \frac{Aa^2b^2(\log a^2 - \log b^2)}{a^2 - b^2}.$$

If Q denotes the volume of fluid which flows through the canal per unit depth in unit time, it is equal to the difference of the value of ψ for $r = a, b$.

$$Q = A(b^2 \log b - a^2 \log a) + B(b^2 - a^2) + C(\log b - \log a)$$
$$= \frac{P}{8\mu\alpha}\left[(a^2 - b^2) - \frac{4a^2b^2}{a^2 - b^2}\left(\log\frac{a}{b}\right)^2\right].$$

If a, b tend to infinity in such a way that $a - b \to d$ and $a\alpha \to l$

$$Q \to \frac{Pd^3}{12\mu l},$$

which agrees with the known result for the flow between parallel planes.

LI. *Theory of Dispersion.*
By Prof. D. N. MALLIK, *Sc.D., F.R.S.E.*[*]

1. **I**T is well-known that the electromagnetic theory, as expressed by the equations of Maxwell and Hertz, cannot account for aberration, dispersion, and allied phenomena. In analysing the reason for this, we note that the theory is based on the following postulates:—

(1) The energy of the electromagnetic field is that of the dielectric medium alone, arising from a certain strained condition of the medium.

(2) The conductors having static charges serve only to limit the dielectric region so that no part of the energy resides on them.

(3) The strained condition of a dielectric is due to electric displacement or polarization f, g, h, subject to the condition

$$\frac{\partial f}{\partial x} + \frac{\partial g}{\partial y} + \frac{\partial h}{\partial z} = 0. \quad \cdots \quad (1)$$

This displacement is apparently held to involve motion of the æther in the medium, subject to a property akin to elasticity (due to inter-action of matter

and æther) defined by the so-called specific inductive capacity of the medium, which thus appears as a constant of the medium.

(4) Conduction as well as convection currents (as in the case of an electrical discharge) involves a tranference ("a procession and not an arrangement" as Faraday put it) dependent on a certain property of the conductor (called its conductivity). This transference is that of electric charge, but what this charge is— whether it is material or æthereal—is not further specified, or is rather left entirely open *.

2. If we limit ourselves to two physical entities, matter and æther, the electric charge whose motion constitutes electric current must be regarded as a mode of manifestation of the æther. If, on the other hand, we agree to regard a unit of electric charge as an actual physical entity, distinct from matter and æther (but related to them and partaking the nature of both in a manner that will require further investigation), we are able to give an account of the various phenomena which are left unexplained on the above postulates.

3. We are led to this additional postulate of a unit of electric charge as a physical entity, not merely on theoretical grounds but as a result of direct experiment. For during electrolysis, each monovalent atom is known to carry with it to the anode a determined quantity of what has hitherto been called a negative electric charge which can be measured and which is independent of the nature of the transported atom. If we assume that this also is the unit charge, which takes part in electric conduction or convection, and if we call it an " electron," we have to conceive a monovalent material atom showing no electrical properties as the result of combination of a single electron with what may fittingly be called one or more units of " positive electricity." This would amount then to the statement that the electrical properties of bodies (as well as those of a dielectric medium) are due to the presence of " electrons " associated with atoms of matter, forming systems of various complexity, and such a theory is found to be consistent with observed facts.

* Maxwell's pronouncement on this point, indeed, clearly sets forth the position (' Electricity and Magnetism,' vol. i.) :

" It appears to me that while we derive great advantage from the recognition of the many analogies between electric current and current of material fluid, we must carefully avoid making any assumption not warranted by experimental evidence, and that there is as yet no experimental evidence to show whether the electric current is really a current of a material substance or a double current, or whether its velocity is great or small as measured in feet per second."

4. Maxwell's remarks [Art. 1 (4) note] had reference to the negative results of the experiments, whereby he proposed to detect in a direct manner the inertia of an electric charge. Experimental determination of the mass of an electron as well as their velocities under certain conditions has supplied the data sought by Maxwell on which to build up the further development of the electromagnetic theory.

5. We have thus justification for regarding the phenomenon of electric conduction in gases as due to "ionization" or generation of charged particles or "ions" which are carriers of electricity.

6. An electric current would then, on this view, consist of two parts—one due to electric displacement which we may still regard as æthereal, and the other due to motion of electrons; or if u is the total current, in the direction of x, we shall have

$$u = \dot{f} + \rho \dot{x}, \quad \ldots \quad \ldots \quad (2)$$

where ρ is the volume density of (free) electrification whose transfer or procession gives rise to convection or conduction current, and $\dot{x}$, its velocity in the direction of x, while $\dot{f} \equiv \dfrac{\partial f}{\partial t}$.

7. Now, when there is free electrification, we must have

$$\frac{\partial f}{\partial x} + \frac{\partial g}{\partial y} + \frac{\partial h}{\partial z} = \rho. \quad \ldots \quad \ldots \quad (3)$$

This must therefore be the further condition satisfied by f, g, h, while in the case of conduction there must, in addition, be a viscous decay which has to be taken account of in a suitable dissipation function.

8. When we proceed to interpret these equations, coupled with the observed phenomena of metallic conduction and dielectric polarization, in terms of the electron theory, we are naturally led to the conclusion that :—

9. A dielectric medium must be conceived to have electrons interspersed in it, giving rise to a constrained (æthereal) motion in the medium defined by the above relation ; this also necessarily imposes a constraint on the motion of electrons. On the other hand, motion of electrons in a conductor must be free (subject however to certain dissipation of energy) so that the static charge in them always resides on the surface.

10. A conception of this kind naturally suggests that the dielectric property of a medium may be explained as arising from the constrained motion imposed on it. We proceed to show that it does, and that in this way we can explain dispersion and allied phenomena.

11. On comparing the equations (1) and (3), we readily see that these cannot be, obviously, satisfied at the same time if f, g, h are to have the same meaning in both.

12. Now if $\rho = 0$, that is in *free æther*,

$$\frac{\partial f}{\partial x} + \frac{\partial g}{\partial y} + \frac{\partial h}{\partial z} = 0.$$

Thus, we may say that in free æther,

$$\frac{\partial f}{\partial x} + \frac{\partial g}{\partial y} + \frac{\partial h}{\partial z} = 0,$$

that in a material medium,

$$\frac{\partial f}{\partial x} + \frac{\partial g}{\partial y} + \frac{\partial h}{\partial z} = \rho,$$

while in all cases,

$$\frac{\partial f_0}{\partial x} + \frac{\partial g_0}{\partial y} + \frac{\partial h_0}{\partial z} = 0, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

where f_0, g_0, h_0 are defined by the equation (4) and are equal to f, g, h, when the medium is free æther.

13. In order to specify these quantities further, we observe that from the equations

$$\frac{\partial f_0}{\partial x} + \frac{\partial g_0}{\partial y} + \frac{\partial h_0}{\partial z} = 0, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

and

$$\frac{\partial f}{\partial x} + \frac{\partial g}{\partial y} + \frac{\partial h}{\partial z} = \rho, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

we may write

$$f_0 = f + A, \text{ &c.}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (5)$$

where

$$\frac{\partial A}{\partial x} + \frac{\partial B}{\partial y} + \frac{\partial C}{\partial z} = -\rho \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (6)$$

14. This expression suggests that A, B, C are components of a quantity I which corresponds to the coefficient of magnetization on the usual theory of magnetism, so that just as $d\mathrm{M} = $ magnetic moment of an elementary magnet $= I d\tau$ (where $d\tau$ is an element of volume), similarly, we may take $d\mathrm{M} = $ electric moment of an element of volume containing electrical charges arising from the presence of electrons and

$$d\mathrm{M} = I d\tau, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (7)$$

where, of course, $I = (A, B, C)$.

15. Again, from (5), we get

$$\dot{f}_0 = \dot{f} + \dot{A}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (8)$$

And if we agree that $\dot{f}_0 = u =$ total current (polarization and convection), we conclude that $\dot{A} = \rho x$, ... (9)

$\dot{x}$, $\dot{y}$, $\dot{z}$ being the velocity of electrons, as before, and it is easily seen that (7) and (9) are consistent, on the understanding that $\rho(x - x_0) = A$ (say) or $e(x - x_0) = A d\tau$,

e being the unvarying charge in vol. $d\tau$,

and $x - x_0 =$ the displacement of e in the direction of x.

Comparing the equations (3), (4), (5), and (6), we conclude that total polarization in any medium may be regarded as made up of two parts—one involving æthereal $(f\,g\,h)$ and the other corpuscular (A B C) displacement.

Again, comparing (8) and (3), we observe that the total current is to be regarded as similarly made up and that it is the total current and total polarization that are subject to the solenoidal condition.

From (6) since, in stationary media,

$$\frac{\partial \dot{A}}{\partial x} + \frac{\partial \dot{B}}{\partial y} + \frac{\partial \dot{C}}{\partial z} + \frac{\partial \rho}{\partial t} = 0,$$

we get the equation of continuity for electrons in motion, viz.:

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho \dot{x}}{\partial x} + + = 0.$$

Again, from (6), we can obviously derive

$$A = \lambda \frac{\partial \phi}{\partial x},$$

where λ is defined by $\lambda \nabla^2 \phi + \rho = 0$.

This equation states that ϕ is the potential of a distribution ρ, provided

$$\lambda = \frac{1}{4\pi} k_0$$

where k_0 is the specific inductive capacity of the medium. Since the medium here is the æthereal medium (whose property is modified by the presence of electrons), k_0 is an absolute constant defining the property of the free æthereal medium.

Thus

$$A = \frac{k_0}{4\pi} \cdot \frac{\partial \phi}{\partial x}, \text{ &c., and } \quad f_0 = f + \frac{k_0}{4\pi} \frac{\partial \phi}{\partial x}; \text{ &c. . (10)}$$

so that

$$f_0 = f + k_0 \frac{e}{4\pi} \frac{\partial}{\partial x} \left(\frac{1}{r} \right),$$

in the neighbourhood of an electric charge, e.

16. On this understanding, the so-called electrostatic energy of the æther will be W_1, where

$$W_1 = \frac{2\pi}{k_0} \int (f^2 + g^2 + h^2) d\tau, \quad \cdots \quad (11)$$

while the potential energy of the material medium will be W, where

$$W = \frac{2\pi}{k} \int (f_0{}^2 + g_0{}^2 + h_0{}^2) d\tau, \quad \cdots \quad (12)$$

while the kinetic energy (T) of a material medium may be taken to be

$$\frac{\mu}{8\pi} \int (\alpha^2 + \beta^2 + \gamma^2) d\tau. \quad \cdots \quad (13)$$

17. From (10) we observe, what is *a priori* evident, that the total force producing the strained condition of the medium is that due to the free æthereal motion and that due to electronic disturbance.

From the expression for W and T, (12) and (13), we get, applying $\delta \int (T - W) d\tau = 0$, where δ is the operator of the calculus of variation, and remembering

$$4\pi \dot{f}_0 = \left(\frac{\partial \gamma}{\partial y} - \frac{\partial \beta}{\partial z} \right), \quad \cdots \quad (14)$$

$$\ddot{f}_0'' = V^2 \nabla^2 f_0, \quad \cdots \quad (15)$$

where $V^2 = \dfrac{1}{k\mu}$.

Hence, since

$$\dot{f}_0' = \dot{f}' + \dot{A}' = \dot{f} + \rho \dot{x}, \quad \cdots \quad (16)$$

and

$$\nabla^2 f_0 = \nabla^2 f + \nabla^2 A = \nabla^2 f + \frac{k_0}{4\pi} \frac{\partial}{\partial x} \nabla^2 \phi, \quad \cdots \quad (17)$$

or

$$\ddot{f}'' + \frac{d}{dt} (\rho \ddot{x}) = V^2 \left(\nabla^2 f - \frac{\partial \rho}{\partial x} \right). \quad \cdots \quad (18)$$

18. Also from Helmholtz's principle we get

$$-\frac{d}{dt} \int (la + mb + nc)\, ds = \int (X dx + Y dy + Z dz), \quad (19)$$

where $a, b, c =$ magnetic induction,

X, Y, Z = electric force.

Hence we have, if

$$X = \frac{4\pi}{k_0} f, \quad (\S\ 21)$$

$$\dot{\alpha} = -4\pi V_0^2 \left(\frac{\partial h}{\partial y} - \frac{\partial g}{\partial z} \right), \quad \text{where } k_0 = \frac{1}{V_0^2}. \quad . \quad (20)$$

(on the understanding that $\mu = 1$), so that V_0 is the velocity of propagation in free æther.

19. From (14), (16), and (21) we get

$$\ddot{\alpha} = -4\pi V_0^2 \left(\frac{\partial \dot{h}}{\partial y} - \frac{\partial \dot{g}}{\partial z} \right) \quad . \quad . \quad . \quad . \quad (21)$$

in stationary media

$$= V_0^2 \left[\nabla^2 \alpha - \frac{\partial}{\partial x} \left(\frac{\partial \alpha}{\partial x} + \frac{\partial \beta}{\partial y} + \frac{\partial \gamma}{\partial z} \right) + \frac{\partial \rho \dot{z}}{\partial y} - \frac{\partial \rho \ddot{y}}{\partial z} \right]. \quad (22)$$

20. Let T_1 = kinetic energy of an electron (e),
$\quad T_2$ = that of the æther,
$\quad V_2$ = potential energy of the æther,
$\quad V_1$ = potential energy due to extraneous forces.

Then since $-f(\beta h - \gamma g) d\tau$ = momentum of the field in the direction of x (J. J. Thomson, ' Recent Researches '),

$$-\frac{d}{dt} \int (\beta h - \gamma g) d\tau + \quad = \frac{d}{dt} \left(\frac{\partial T_2}{\partial \dot{x}} \right),$$

x, y, z defining the position of an electron.

Applying the Lagrangian equations of motion for the system consisting of the æther and the electron, viz.:

$$\frac{d}{dt} \left(\frac{\partial T_1}{\partial \dot{x}} + \frac{\partial T_2}{\partial \dot{x}} \right) - \frac{\partial (T_1 + T_2)}{\partial x} + \frac{\partial (V_1 + V_2)}{\partial x} = 0,$$

we get

$$\frac{d}{dt} \left(\frac{\partial T_1}{\partial \dot{x}} \right) + \frac{\partial V_1}{\partial x} = \frac{\partial T_2}{\partial x} + \frac{d}{dt} \int (\beta h - \gamma g) d\tau - \frac{\partial V_2}{\partial x}$$

since

$$\frac{\partial T_1}{dx} = 0, \text{ obviously.}$$

i.e. $\quad \dfrac{d}{dt} \left(\dfrac{\partial T_1}{\partial \dot{x}} \right) + \dfrac{\partial V_1}{\partial x} = \int (h\dot{\beta} - g\dot{\ })d\tau + \int (\beta \dot{h} - \gamma \dot{g})d\tau + \dfrac{\partial T_2}{\partial x} - \dfrac{\partial V_2}{\partial x}$

$$= -\frac{4\pi}{k_0} \int \left[\left(\frac{\partial f}{\partial z} - \frac{\partial h}{\partial x} \right) h - \left(\frac{\partial g}{\partial x} - \frac{\partial t}{\partial y} \right) g \right] d\tau - \int \left[\beta (\omega - \rho \dot{z}) - \gamma (v - \rho \dot{y}) \right] d\tau$$

$$+ \frac{\partial T_2}{\partial x} - \frac{\partial V_1}{\partial x}, \quad . \quad . \quad . \quad . \quad . \quad (23)$$

since
$$-\beta' = \frac{4\pi}{k_0}\left(\frac{\partial f}{\partial z} - \frac{\partial h}{\partial n}\right)$$

$$\omega = \dot{h} + \rho\dot{z}, \text{ \&c. } [\S 6].$$

Integrating by parts the first integral of (23) and substituting

$$4\pi\omega = \frac{\partial\beta}{\partial z} - \frac{\partial\gamma}{\partial y} \text{ \&c.}$$

in the second integral and again integrating by parts, we get

$$\frac{d}{dt}\left(\frac{\partial T_1}{\partial\dot{x}}\right) + \frac{\partial V_1}{\partial x} = \frac{4\pi}{k_0}\int f\left(\frac{\partial f}{\partial x} + \frac{\partial g}{\partial y} + \frac{\partial h}{\partial z}\right)d\tau - \frac{\partial T_2}{\partial x} + \frac{\partial T_2}{\partial x}$$

$$+ \int \rho(\dot{y}\gamma - \dot{z}\beta)d\tau + \frac{\partial V_2}{\partial x} - \frac{\partial V_2}{\partial x}$$

$$= \frac{4\pi}{k_0}\int \rho f\,d\tau + \int \rho(\dot{y}\gamma - \dot{z}\beta)d\tau, \quad . \quad . \quad . \quad (24)$$

which may be stated in words as follows :—

An electron in motion is subjected to a force which is the sum of an electrostatic force and an electrodynamic force, as the result of the action of the field. [Poincaré, 'Électricité et optique.']

21. Again, if T_2 be the kinetic energy of free æther, we have

$$T_2 = \int (Fu + Gv + Hw)d\tau,$$

where $u = \dot{f} + \dot{A}$, &c.,

while W = the potential energy

$$= \frac{2\pi}{k_0}\int (f^2 + g^2 + h^2)d\tau, \text{ where it should be remembered}$$

$k_0 = \dfrac{1}{V_0^2}$, V_0 being the velocity of light in free æther, and

f, g, h are connected by the equation of condition

$$\frac{\partial f}{\partial x} + \frac{\partial g}{\partial y} + \frac{\partial h}{\partial z} = \rho.$$

Introducing (in the manner of Larmor) an undetermined multiplier ϕ and writing

$$W' = \frac{2\pi}{k_0}\int (f^2 + g^2 + h^2)d\tau - \int \phi\left[\left(\frac{\partial f}{\partial x} + \ldots\right) - \rho\right]d\tau,$$

we have

$$\delta W' = \frac{4\pi}{k_0}\int (f\delta f + \dots)d\tau - \int \phi\left[\frac{\partial \delta f}{\partial x} + + \right) - \delta\rho\right]d\tau, \quad (25)$$

since ϕ is not to vary. Now integrating by parts into surface (s) integrals and volume integral, we have

$$\delta W' = \int\left\{\left(\frac{4\pi}{k_0}f + \frac{\partial\phi}{\partial x}\right)\delta f + +\right)d\tau + \int\phi\delta\rho d\tau - \int\phi(lf + +)ds.$$

Now from the Lagrangian equation (since f, g, h may be taken as generalized coordinates)

$$\frac{d}{dt}\frac{\partial T_2}{\partial \dot{f}} - \frac{\partial T_2}{\partial f} + \frac{\partial W'}{\partial f} = 0,$$

or

$$\dot{F} + \frac{4\pi}{k_0}\dot{f} + \frac{\partial\phi}{\partial x} = 0, \quad . \quad . \quad . \quad . \quad (26)$$

where ϕ is evidently the potential of distribution ρ.

That is (if the medium is at rest) the electrostatic force due to the medium (say X)

$$= -\dot{F} - \frac{\partial\phi}{\partial x}$$

(the latter of which is due to ρ) on the understanding that

$$\frac{4\pi}{k_0}f = X.$$

22. It will be observed that k of the ordinary electro-magnetic theory becomes k_0. This amounts to the postulate that there is no dielectric other than free æther.

Remembering that

$$A = \frac{k_0}{4\pi}\frac{\partial\phi}{\partial x},$$

we conclude that

$$\dot{F} = -\frac{4\pi}{k_0}\dot{f}_0.$$

23. Returning to the equation (24), we observe that $-\dfrac{\partial V}{\partial x} =$ the force due to the system of electrons in volume $\int d\tau +$ the force brought into play on account of the displacement of electrons.

If we take a small sphere of the volume $\int d\tau$, the system of

electrons defined by $\dfrac{\partial A}{\partial x} + \dfrac{\partial B}{\partial y} + \dfrac{\partial C}{\partial z} = -\rho$ may be replaced by a surface distribution $I\cos\theta$, per unit area of spherical surface. And thus, as in the corresponding magnetic theory, this part of the force in the direction of x will be $\dfrac{4}{3}\pi\dfrac{A}{k_0}$ per unit charge [Maxwell, vol. ii. art. 399]. For the second force we may, obviously, assume an elastic force in the direction of x, due to displacement of electron, and this will be

$$-\mu(x - x_0)\ (\text{say}) = -\mu\frac{A}{\rho}, \quad \ldots \quad (27)$$

while the frictional force will be of the form $\lambda \dot{A}'$. Hence, for equilibrium

$$\frac{\mu \int A d\tau}{\int \rho d\tau} = \frac{4\pi}{k_0}\int \rho\left(f + \frac{A}{3}\right)d\tau + \int \rho(\dot{y}\gamma - \dot{z}\beta). \quad (28)$$

Putting

$$\mu = \frac{4\pi}{k_0}\mu_0, \qquad \int A dt = \overline{A}, \qquad \int \rho f\,d\tau = \overline{ef},\ \&\text{c.,}$$

we have

$$\mu_0 \overline{A} = e^2(\overline{f} + \tfrac{1}{3}\overline{A}) + \frac{k_0}{4\pi}e^2\,(\overline{\dot{y}\gamma} - \overline{\dot{z}\beta}), \quad \ldots \quad (29)$$

or for simplicity

$$\mu_0 A = e^2(f + \tfrac{1}{3}A) + \frac{k_0}{4\pi}e^2\,(\dot{y}\gamma - \dot{z}\beta), \quad \ldots \quad (30)$$

all the quantities having their mean values taken over a small sphere, enclosing a charge.

For motion, we have $\rho\ddot{x} = \ddot{A}$,

or

$$\int \ddot{x}\rho\,d\tau = \ddot{A}, \quad \ldots \ldots \quad (31)$$

where for $\ddot{A}$ we take its mean value, as before.

Accordingly, since for a single electron of mass m, self-inductance L, and charge e,

$$T = \tfrac{1}{2}(m + Le^2)(\dot{x}^2 + \dot{y}^2 + \dot{z}^2), \quad \ldots \quad (32)$$

we have

$$\frac{4\pi}{k_0}\mu_0 A + (Le^2 + m)\ddot{A} = \frac{4\pi}{k_0}e^2\left(f + \frac{A}{3}\right) + e^2(\dot{y}\gamma - \dot{z}\beta)$$

$$= \frac{4\pi}{k_0}e^2\left(f + \frac{A}{3}\right) + e^2(\gamma\dot{B} - \beta\dot{C}). \quad (33)$$

Writing

$$L e^2 + m = \lambda$$

$$\frac{4\pi}{k_0} \mu_0 - \frac{4\pi}{k_0} \frac{e^2}{3} = p_0^2 \lambda$$

$$\frac{4\pi}{k_0} e^2 = a_0 \lambda, \qquad \qquad \right\} \quad . \quad . \quad . \quad . \quad (34)$$

we get

$$\ddot{A} + p_0^2 A = a_0 f, \ \&c. \quad . \quad . \quad . \quad (35)$$

if the magnetic field is weak, and

$$\ddot{f} + \ddot{A} - V^2 \Delta^2 f = V^2 \frac{\partial \rho}{\partial x} \quad \text{from (18).} \quad . \quad . \quad (36)$$

From (35) we deduce

$$\ddot{\rho} + (p_0^2 + a_0)\rho = 0 \right\} \quad . \quad . \quad . \quad . \quad (37)$$

$$\therefore \ \rho = \rho_0 a_0 \cos (mt + \epsilon) \left\}$$

24. If $\frac{\partial \rho_0}{\partial x} = 0$, or ρ_0 is independent of coordinates, the equations will be

$$\ddot{A} + p_0^2 A = a_0 f \right\} \quad . \quad . \quad . \quad . \quad (38)$$

$$\ddot{f} + \ddot{A} - V^2 \Delta^2 f = 0 \left\}$$

For a plane wave $(z = \text{const.})$, $\Delta^2 f = \frac{d^2 f}{dz^2}$, &c.

and the solution is

$$A = A_0 \, e^{ip} \left(\frac{nz}{V} - t \right)$$

$$f = f_1 \, e^{ip} \left(\frac{nz}{V} - t \right),$$

which yield

$$n^2 = 1 + \Sigma \frac{a_k}{p_0^2 - p_k^2}, \quad . \quad . \quad . \quad . \quad (39)$$

where n is the index of refraction and $\frac{2\pi}{p_0} = $ the periodic time of vibrations of electrons unaffected by the field, while Σ refers to the several groups of electrons that are set vibrating on account of the impressed disturbance.

25. Returning to equation (35), and introducing a viscous term $b_0 \dot{A}$ we get

$$\ddot{A} + b_0 \dot{A} + p_0^2 A = a_0 f. \quad . \quad . \quad . \quad (40)$$

Now, assuming the solutions

$$A = A_0 \, e^{ir}\left(\frac{nz}{V} - t\right)$$

$$f = f_1 \, e^{ip}\left(\frac{nz}{V} - t\right),$$

we get

$$n^2 = 1 + \Sigma \frac{a_k}{p_0^2 - ipb_0 - p_k^2},$$

showing that there is absorption in this case.

If p_0 is very nearly equal to p, b_0 cannot be neglected ; this further indicates that there is always absorption, under these circumstances.

If p is very small, then $n^2 = n_0^2 + \dfrac{a_0}{p_0^2 - ipb_0}$ and the real part of n is

$$n_0\left(1 + \frac{cp_0^2}{p_0^4 + p^2 b_0^2}\right), \text{ where } a_0 = zn_0^2 c.$$

As p increases n diminishes. This explains anomalous dispersion.

26. It is not without interest to compare the above with the various elastic solid theories that have been proposed for the explanation of dispersion.

27. For this, let us recall the fact that in an elastic medium there is, associated with an elastic displacement, molecular rotation ; and if the properties of the medium are to be capable of being expressed in terms of quantities that enter into the statement of either theory, electric displacement and magnetic force must correspond in some way with the velocity of vibration and molecular rotation. Now in the electrical theory we have two quantities defining the property of the medium μ and k, as well as the quantities f, g, h (polarization) and H (magnetic force), while in the theory of elasticity we have the constants ρ (density), n (rigidity), and the quantities ω (molecular rotation) and $\xi \, \eta \, \zeta$ (displacement), and it will be necessary to decide upon a suitable mode of identifying these, severally.

28. Now, on examining the expression for energy (kinetic and potential) in terms of these two sets of quantities, it is easy to see that one such mode of establishing a concordance between the two sets of phenomena is (as Larmor has done) to identify electric displacement with molecular rotation and magnetic force with æthereal velocity (in vibratory motion).

On this theory, the electrostatic energy

$$\frac{2\pi}{k} \int (f_0^2 + g_0^2 + h_0^2) d\tau$$

will correspond to the energy of strain of an elastic medium, since this is

$$= 2n \int (\omega_x^2 + \omega_y^2 + \omega_z^2) d\tau + \text{surface integrals if } \left(k + \frac{4}{3} n \right) \Delta = 0,$$

so that on this theory we have

$$\frac{2\pi f_0^2}{k} = 2n\omega_x^2, \text{ &c. (13), and } \frac{1}{k\mu} = \frac{n}{\sigma}, \quad . \quad . \quad (41)$$

provided we further postulate the identity of the kinetic energy of a strained elastic medium, viz.:

$$\tfrac{1}{2} \int \sigma(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) d\tau,$$

and electromagnetic energy

$$\frac{1}{8\pi} \int \mu(\alpha^2 + \beta^2 + \gamma^2) d\tau,$$

where $\sigma =$ density of the medium,

$\xi = x - x_0$, &c. $=$ elastic displacements of the medium,

$\alpha, \beta, \gamma =$ magnetic force,

$\omega_x, \omega_y, \omega_z =$ molecular rotation.

29. From (13) we derive, provided $\dfrac{\mu}{\sigma} =$ constant,

$$2\pi f_0^2 = \omega_0^2,$$

and this leads to the conclusion that the resultant twist is made up of an æthereal motion in addition to an electronic displacement, neither of which is however of the nature of a pure rotation by itself.

30. We are now in a position to consider the equations of motion that have been proposed[*] to explain dispersion. Boussinesq's formula is

$$m\frac{d^2u}{dt^2} + \mu\frac{d^2U}{dt^2} = \left(k + \frac{4}{3} n \right) \frac{\partial \Delta}{\partial x} + n\Delta^2 u,$$

where m is the mass, u the displacement of the æther, and μ, U, those of " matter," and $k =$ volume elasticity, &c.

[*] Glazebrook, B. A. Report, 1885.

31. From these we may easily derive the corresponding rotational equations, viz.:

$$m\ddot{\omega}_x + \mu\ddot{\Omega}_u = n\nabla^2\omega_x, \quad \ldots \ldots \text{(42)}$$

where ω_x, Ω_x are the curls of $u, v, w, \mathrm{U}, \mathrm{V}, \mathrm{W}$. Boussinesq's theory is thus seen to be capable of being interpreted as being based on the postulate of twists, defining the disturbed state of the medium.

For, if we write

$$\omega_x + \frac{\mu}{m}\,\Omega x = f + \mathrm{A} = f_0,$$

we get, putting $\frac{n}{m} = c^2$,

$$\ddot{f} + \ddot{\mathrm{A}} = c^2\Delta^2 f,$$

provided $\Delta^2(\Omega x - \mathrm{A}) = 0. \quad \ldots \ldots \text{(43)}$

Now $\nabla^2\mathrm{A} = \dfrac{k_0}{4\pi}\dfrac{\partial}{\partial x}\nabla^2\phi = \dfrac{k_0}{4\pi}\dfrac{\partial\rho}{\partial x} = 0.$

Further, the equation of equilibrium of a material medium regarded as an elastic body would be $\nabla^2\Omega x = 0$, &c., so that (43) amounts to the statement that in forming the equation of motion we must regard the material medium to be at rest.

Again, U and u are assumed by Boussinesq to be connected by an equation of the form $\mathrm{U} = f(u)$, and in particular, for dispersion, U is taken by Boussinesq

$$= \lambda u + \mathrm{C}\frac{\partial\Delta}{\partial x} + \mathrm{D}\nabla^2 u, \text{ where } \lambda, \mathrm{C}, \mathrm{D} \text{ are constants;} \quad \text{(44)}$$

whence on our notation,

$$\Omega x = \lambda\omega_x + \mathrm{D}\nabla^2\omega_x, \text{ &c.,} \quad \ldots \ldots \text{(45)}$$

or

$$\mathrm{A} = f + \mathrm{D}\frac{\ddot{f} + \ddot{\mathrm{A}}}{c^2} \text{ where } 2f = \omega_x(1+\lambda) + \Omega x\left(\frac{\mu}{n} - 1\right). \quad \text{(46)}$$

If we admit that f is an harmonic function, the equation can obviously be written in the form

$$\ddot{\mathrm{A}} + p_0 = a_0 f, \quad \ldots \ldots \ldots \text{(47)}$$

the constants being suitably adjusted.

32. The equations of Helmholtz with the same notation as in §30 are

$$m\ddot{u} = \alpha^2 \nabla^2 u + \beta^2 (U - u)$$

and

$$\mu \ddot{U} = -\beta^2 (U - \alpha) - \alpha^2 U - \gamma^2 \dot{U}, \quad \Big\} \quad . \quad (48)$$

whence

$$m\ddot{\omega}_x = \alpha^2 \nabla^2 \omega_x + \beta^2 (\omega_x - \Omega_x)$$

$$\mu \ddot{\Omega}_x = \beta^2 (\Omega_x - \omega_x) - \alpha^2 \Omega_x - \gamma' \dot{\Omega}_x. \quad \Big\} \quad . \quad (49)$$

On transformation, for purposes of comparison with the electron theory, *i. e.* putting

$$\omega_n = \lambda f + \nu A, \qquad \Omega_u = \lambda' f + \nu' A, \quad . \quad . \quad (50)$$

we get

$$m(\lambda \ddot{f} + \nu \ddot{A}) = \alpha^2 \nabla^2 (\lambda f + \nu A) + \beta^2 \{ (\lambda - \lambda') f + (\nu - \nu') A \}, \quad (51)$$

and

$$\mu(\lambda' \ddot{f} + \nu' \ddot{A}) = \beta^2 [(\lambda' - \lambda) f + (\nu' - \nu) A] - \alpha^2 (\lambda f + \nu' A)$$
$$- \gamma^2 (\lambda' \dot{f} + \nu' \dot{A}). \quad . \quad . \quad (52)$$

The equation (52) is the same as the equation (48) provided $\lambda' = 0$, while from (51) we get (if $\lambda' = 0$) an equation of the form

$$\ddot{f} + \ddot{A} = \alpha'^2 \nabla^2 f + \beta'^2 f + \gamma'^2 A.$$

Remembering that f and A must vary as $\cos pt$ (say) we can obviously adjust the constants and variables so as to put the above equation in the form

$$\ddot{f} + \ddot{A} = \alpha'''^2 \nabla^2 f,$$

which is the second equation (38). [A and f differing in value from the same quantities occurring in (51) and (52) each by a constant factor.]

33. Kettler's equations are of the form (Glazebrook's notation)

$$m\ddot{u} + \mu C'' \ddot{U} = \alpha^2 \nabla^2 u$$

$$\mu C \ddot{u} + \mu'' \ddot{U} = -\alpha^2 \ddot{U} - \beta^2 \ddot{u}, \quad \&c.$$

which yield as before

$$m\ddot{\omega}_x + \mu C'' \ddot{\Omega}_x = \alpha^2 \nabla^2 \omega_x$$

$$\mu C \ddot{\omega}_x + \mu \ddot{\Omega}_x = -\alpha^2 \Omega_x - \beta^2 \ddot{\Omega}_x, \quad \&c.,$$

which are the same equations as (51) and (52), if we put

$$m\omega_x + \mu C' \Omega_x = f + A \quad \text{and} \quad \mu C \omega_x + \mu \Omega_x = \lambda f + \nu A.$$

On eliminating f and putting $\lambda m - \mu c = 0$ these yield

$$\ddot{f} + \ddot{A} = \nabla^2 f \quad \text{and} \quad C\ddot{A}'' + \ddot{f}'' = a_1^2 A + a_2^2 \dot{A}.$$

And if f varies as $\cos pt$, these equations are of the same form as (38).

34. Inasmuch, however, as

$$\frac{\partial A}{\partial x} + \frac{\partial B}{\partial y} + \frac{\partial C}{\partial z} = -\rho$$

and

$$\frac{\partial f}{\partial x} + \frac{\partial g}{\partial y} + \frac{\partial h}{\partial z} = \rho,$$

(A, B, C) and (f, g, h) cannot be interpreted as rotations, each by itself, and to that extent these theories are less general than the electron theory.

The main difference, however, consists really in the fact that the elastic solid theories deal with æther and matter, while the electron theory deals with æther and electron.

35. In attempting a comparison between the elastic solid theory and the electron theory, we have identified the electrostatic energy with the energy of (rotational) strain of the elastic medium, and the electromagnetic energy with its kinetic energy.

36. But the identification is not unique, as we do not know which of the two expressions (in either system) is kinetic or which potential, or in fact whether both the energies are not (as they most likely are) kinetic. We may, therefore, if we like [*], regard electric force as identical with the rate of elastic displacement and magnetic force with molecular rotation.

37. On this scheme, the electromagnetic energy

$$\frac{1}{8\pi} \int \mu (\alpha^2 + \beta^2 + \gamma^2) d\tau$$

is to be identified with the energy of strain

$$\int 2n (\omega_x^2 + \omega_y^2 + \omega_z^2) d\tau,$$

provided we have

$$\left(k + \frac{4}{3} n \right) \Delta = 0,$$

* Glazebrook's Address as President of the Physical Section, B. A. 1893.

which yields the solenoidal condition for magnetic induction, viz. :

$$\frac{\partial a}{\partial x} + \frac{\partial b}{\partial y} + \frac{\partial c}{\partial z} = 0,$$

since

$$\frac{\partial \omega_x}{\partial x} + \frac{\partial \omega_y}{\partial y} + \frac{\partial \omega_z}{\partial z} = 0,$$

(provided $n\mu$ is constant).

38. When we proceed to identify the kinetic energy

$$\tfrac{1}{2}\sigma \int (u^2 + v^2 + w^2) d\tau$$

of the elastic medium with the electrostatic energy, we observe that if the elastic medium is æthereal, the equation of condition should be

$$\tfrac{1}{2}\sigma_0 \int (u_0^2 + v_0^2 + w_0^2) d\tau = \frac{2\pi}{k_0} \int (f^2 + g^2 + h^2) d\tau,$$

while if the medium is a material medium we must have

$$\tfrac{1}{2}\sigma \int (u^2 + v^2 + w^2) d\tau = \frac{2\pi}{k} \int (f_0^2 + g_0^2 + h_0^2) d\tau.$$

These yield the following results :—

$$\sqrt{k_0\mu} = \frac{\sigma_0}{n} = \frac{1}{V_0^2},$$

where V_0 is the velocity of light in the æther;

$$\sqrt{k\mu} = \frac{\sigma}{n} = \frac{1}{V^2},$$

where V is the velocity of light in any medium $(\sigma, n$ or $k, \mu)$. Also

$$\dot{\Delta}\left(\equiv \frac{d\Delta}{dt}\right) = \frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z} = \frac{1}{k_0}\left(\frac{\partial f}{\partial x} + \frac{\partial g}{\partial y} + \frac{\partial h}{\partial z}\right) = \frac{\rho}{k_0},$$

where Δ is the dilatation of the medium.

Also

$$\frac{\partial u}{\partial x} + + = \frac{\partial f_0}{\partial x} + + = 0,$$

i. e. the total displacement (æthereal and electronic) is solenoidal, while the volume density of electricity is proportional to æthereal expansion.

39. The various equations appropriate to an elastic medium are then found to have their analogies in the electric theory.

Thus the equation

$$\left(k + \tfrac{4}{3}n\right)\frac{\partial \Delta}{\partial x} - 2n\left(\frac{\partial w_z}{\partial y} - \frac{\partial w_y}{\partial z}\right) = \sigma\ddot{\xi}$$

yields the electrostatic equation for a material medium, in the form

$$\dot{f_0} = \mathrm{V}^2\left(\frac{\partial \gamma}{\partial y} - \frac{\partial \beta}{\partial z}\right)$$

on *properly choosing the signs.*

40. The equation of motion of such a medium, viz. :

$$\ddot{\xi} = \mathrm{V}^2\nabla^2\xi,$$

yields $$\dddot{\xi} = \mathrm{V}^2\nabla^2\dot{\xi}$$

or $$\dddot{f_0} = \mathrm{V}^2\nabla^2\dot{f_0},$$

i. e. $$\ddot{f} + \ddot{\mathrm{A}} = \mathrm{V}^2\nabla^2(\,\dot{f} + \mathrm{A}) = \mathrm{V}^2\nabla^2\dot{f},$$

if $$\nabla^2\mathrm{A} = 0,$$

while for the *free* æthereal medium we have

$$\ddot{f} = \mathrm{V}_0{}^2\nabla^2\dot{f},$$

41. Again Boussinesq's equation, viz.,

$$\sigma_0\dot{u}_0 + \rho_1\dot{\mathrm{U}} = n\nabla^2\xi, \quad \text{yields,}$$

if we put $\sigma_0 u = \dot{f}$ and $\rho_1\mathrm{U} = \dot{\mathrm{A}}$, $\dfrac{n}{\sigma_0} = \mathrm{V}_0{}^2$,

$$\ddot{f} + \ddot{\mathrm{A}} = \mathrm{V}_0{}^2\nabla^2\dot{f}.$$

The other equation of condition of Boussinesq, viz.,

$$\mathrm{V} = \lambda u + \mathrm{C}\frac{\partial \Delta}{\partial x} + \mathrm{D}\nabla^2 u,$$

gives similarly $$\dot{\mathrm{A}} = \lambda' \dot{f} + \mathrm{D}'\nabla^2\dot{f}$$

$$= \lambda' \dot{f} + \mathrm{D}'\frac{\ddot{f} + \ddot{\mathrm{A}}}{\mathrm{V}_0{}^2},$$

and similarly for the equations of Helmholtz and Ketteler.

42. A third method of identification will be to take

$$(\omega_x, \omega_y, \omega_z) = (\alpha, \beta, \gamma), (\xi_0{}^{\cdot}, \eta_0{}^{\cdot}, \zeta_0{}^{\cdot}) = (f, g, h) \text{ and } \xi^{\cdot}, \eta^{\cdot}, \zeta^{\cdot}) = (f_0, g_0, h_0)$$

giving

$$\frac{\partial \alpha}{\partial x} + \frac{\partial \beta}{\partial y} + \frac{\partial \gamma}{\partial z} = 0,$$

as in the electronic theory, $\Delta = \rho$, while all other equations are practically the same as before.

43. Now electrical experiments lead to the conclusion that μ is very nearly constant in a dielectric, but that k varies, while optical experiments make the constancy of n and variability of ρ probable, so that the second mode of representation would appear at first sight to be more in accordance with facts. It seems, however, that except in so far as the identification of the constants is concerned, the question of interaction of matter and æther is resolvable on any of these hypotheses, for we may simply have $\dfrac{n}{\sigma} = \dfrac{1}{k\mu} = V^2$, where V is the velocity of propagation, although it may not be possible to identify separately the various quantities, that enter in these investigations, according to any of the schemes tabulated above. On this understanding, it does not seem to be possible to pronounce in favour of any of these in preference to the others. In spite of the uncertainty that exists in this respect, these various modes of representation are useful, as we have so little knowledge of the intimate nature of electric and magnetic quantities.

LII. *The Average Thorium Content of the Earth's Crust.* *By* J. H. J. Poole [*].

THIS series of experiments was undertaken with the view of supplementing a previous paper of Dr. Joly's on the "Radioactivity of Terrestrial Surface Materials," which appeared in the Philosophical Magazine for October 1912. The same composite rock mixtures as were used in the previous series of experiments were also used in these.

The method of procedure and the design of the apparatus have been fully described by him in the Philosophical Magazine for May 1909. It may be briefly said that the rock has first to be got into solution by fusing it with a mixture of the alkaline carbonates; either a blowpipe or a small electric furnace being used for this purpose, as a

temperature of about 1000° C. is requisite. The melt is then treated with water and filtered. The filtrate is discarded as it has been found to contain only a negligible quantity of thorium. The residue left on the filter-paper is dissolved in distilled water containing 50 c.c. of pure HCl, and the solution made up to a convenient bulk with added distilled water. This solution is set aside for some days to allow the thorium disintegration products time to grow, as some of them are lost in the process of getting the rock into solution. The thorium content is determined by boiling off the thorium emanation in a constant stream of air, which air then passes through an ordinary gold-leaf electroscope. By determining the rate of leak of the electroscope when the solution is boiling and when it is not, we can estimate the amount of thorium in the solution. The solution before being tested is boiled in a separate vessel to drive off the radium emanation if there is any present.

The electroscope is standardized with a thorianite solution of known strength, as Dr. Joly has previously described. One c.c. of this solution was either added to a known amount of distilled water or to a rock solution whose relative activity had already been determined. In either case, by observing the new rate of leak we can easily calculate what quantity of thorium corresponds to a gain of rate of leak of one scale-division per hour.

The latter method was adopted to see whether rock solutions had the power of concealing, as it were, the emanation that they contained. If this were the case, one would expect a higher constant for the electroscope to be obtained by the second method. However, by both methods a practically identical value was obtained. The whole method is of course only a comparative one, the effect of any rock solution being compared with that of the standard. For this reason great care has to be taken to keep the conditions under which the standard solution and the rock solution are boiled as similar as possible. In all cases some powdered steatite has to be added to the solution to make it boil freely and to prevent bumping. Many solutions were found to be very sensitive to any change in the form of ebullition, and in these cases it was often necessary to add some fresh steatite, as the steatite after a certain time lost its power of producing free ebullition.

The constant of the electroscope depends largely on the rate of the draught of air through the boiling flask, and thence through the condenser and electroscope. There is one rate of flow which gives the lowest constant for the

I. Acid Rocks.

Composite.	Ra grm. per grm. $\times 10^{12}$.	Thorium grm. per grm. $\times 10^5$.		Ratio Ra/Th $\times 10^7$	
		(1)	(2)		
63 Granites	2·7	2·04	2·00	1·33	
23 Acid Intrusive & Volcanic ...	3·9	2·31	...	1·73	
Ditto New Solution	...	...	2·20	...	

Mean for 86 rocks $= 2\cdot05 \times 10^{-5}$

II. Intermediate Rocks.

Composite.	Ra grm. per grm. $\times 10^{12}$.	Thorium (1)	Thorium (2)	Ratio Ra/Th $\times 10^7$	
12 Syenites :					
(1) 10 grms. in solution	2·4	4·08	...	0·59	
(2) 6 grms. in solution	...	...	1·75	1·37	
(3) 5 grms. in solution............	...	...	1·68	1·47	
6 of the above Syenites	...	...	4·2	0·57	
8 Diorites	1·6	0·99	...	1·62	
18 Trachytes...........................	3·0	1·79	...	1·68	
10 Porphyries	2·8	1·54	...	1·82	

Mean for 48 rocks $= 1\cdot64 \times 10^{-5}$

III. Basic Rocks.

Composite.	Ra grm. per grm. $\times 10^{12}$.	Thorium (1)	Thorium (2)	Ratio Ra/Th $\times 10^7$	
11 Basalts (chiefly Hebridean) ...	0·5	0·38	...	1·28	
5 Gabbros	1·3	0·50	...	2·6	
8 Diabases and Dolerites	1·0	0·22	...	4·55	
14 Basalts and Melaphyres	2·0	0·84	...	2·38	
18 General Basalts	1·4	0·63	0·63	2·22	
Ditto New Solution..............	...	...	0·56	2·50	

Mean for 56 rocks $= 0\cdot56 \times 10^{-5}$

IV. Miscellaneous Rocks.

Composite.	Ra grm. per grm. $\times 10^{12}$.	Thorium (1)	Thorium (2)	Ratio Ra/Th $\times 10^7$	
7 Vesuvian Lavas	12·6	2·36	...	5·34	
14 Gneisses	2·1	0·87	...	2·42	
6 Deccan Traps	...	...	0·47		
Globigerina Ooze					
56 per cent. soluble in HCl ...	...	...	0·0		
44 per cent. insoluble ,, ...	...	...	0·28†		
All in one solution..............	...	...	0·36		
Krakatoa Ash :					
Sol. I.	...	...	0·8		
Sol. II.	...	...	0·9		
Sol. III.	...	...	1·0		

† This is per grm. of Globigerina Ooze.

NOTE.—(*a*) The results given under column (1) for the thorium content
were obtained while working with the higher constant, while
those in column (2) were obtained with the lower constant.
    (*b*) Krakatoa Ash. In solution I. and solution II. 2 grms. of
$KClO_3$ were added to the fusion mixture. 100 c.c. of HCl were
used in solution II. instead of 50 c.c. Solution III. was made
in the usual way.

instrument, for if the draught is too fast the emanation will only be left in the electroscope for a very short time, and hence it will only produce a small effect; but if, on the other hand, the draught is too slow, most of the emanation will have died out before the air reaches the electroscope at all, and so in this case also the effect will be small.   Some of the results given were obtained when the instrument had a higher constant than in the subsequent experiments.   The higher constant had a value of $3 \cdot 2 \times 10^{-5}$, while the subsequent lower one was $2 \cdot 1 \times 10^{-5}$.   The change in constant was due to the draught through the instrument being altered. The results obtained with the constants are shown separately in the table of results.   It will be seen that whenever a solution was retested with the lower constant, the new result obtained agreed fairly well with the old.   This is a satisfactory feature of the experiments.

Dr. Joly has described, in his previous paper, how the composite rock mixtures were originally made.   Amounts of the rock mixtures varying from five to fifteen grams were used in the solutions.   The smaller amounts were generally only used in the repeat experiments owing to a certain scarcity of material.   One advantage, however, of varying the amount of rock in the solution is that it would show if any contamination of the solutions had occurred, as we would expect a higher value for the thorium content of the weaker solution if we assume that in each solution there was the same absolute amount of contamination approximately. Anyway it would seem justifiable to assume that there could not be any large amount of contamination if the two solutions gave nearly the same result, as it appears highly improbable that each solution should be contaminated in exact proportion to the amount of rock it contained.   This argument of course does not apply to any contamination which the original powder as a whole may have received.   Ordinary incandescent gas-mantles are a very dangerous source of contamination, and accordingly their presence in the laboratory should be avoided.

The composite rock mixtures used may be roughly divided into three classes, *i. e.* acid, intermediate, and basic.   Some results obtained for some miscellaneous rocks are also given. For the sake of comparison the radium content of these rocks, as determined by Dr. Joly by the electric furnace method, are also given.   It will be seen from the results that the thorium content decreases as we pass from acid to basic rocks.   In this respect the thorium content resembles the radium content.   However, there is no exact numerical

proportion existing between the two, as will be seen from the figures. There is nevertheless a certain amount of evidence that the ratio of radium to thorium also increases as we pass from the acid to the basic rocks, and for certain rocks this ratio seems to remain fairly constant. It is also remarkable that the value of the ratio always lies within such narrow limits. In only three or four cases does it lie outside the range 1·3 to 2·7 × 10^{-7}. This range is perhaps not narrow enough to justify us in assuming that there might be any genetic connexion between uranium and thorium, but that the ratio is as constant as it is, is certainly a remarkable fact.

The mixture of the twelve syenites gave rather confusing and disconcerting results. Dr. Joly first determined its activity using a solution containing 10 grms. of the mixture, and obtained a result of 4·08 × 10^{-5} grm. of thorium per gram of rock. He thought that this result was rather high, and suspected that the solution had been contaminated, so two new solutions, one containing six grams and the other five, were made up. Both these solutions gave a value for the thorium content of approximately 1·7 × 10^{-5}. This result would naturally lead us to suppose that the first solution had been contaminated as first thought. Unfortunately for this theory, however, when a solution containing six grams of a mixture of only six of the original syenites was tested by the present writer, it gave a result of 4·2 × 10^{-5}. It is hard to explain how the two solutions that gave the high results could both have been contaminated to proportional amounts so that they would give nearly the same result. The discordance between the values might possibly be explained by assuming that the thorium in some of the syenites was not evenly distributed through the rock, so that the powder would contain specks of highly active matter. In this case, we could understand that in one case we might by some chance get a good deal more of these particles than in another, and so obtain a higher result. This theory is however incomplete, as it fails to explain the fact that the activity of the mixture seems to possess two fairly definite values, namely, 1·7 and about 4·1 × 10^{-5}. It might be thought that the second high value could be explained by the fact that the mixture only contained six syenites. It seems, however, that this cannot be done, as even if we assume that the six syenites rejected in making up the solution contain no thorium at all, still even in this extreme case we ought to obtain a value for the thorium content of only double the value for the twelve syenites. This value would be about 3·4 × 10^{-5}, which is appreciably lower than the actual result

obtained. It is of course highly improbable that the thorium would be distributed in the way assumed. It is more likely that both the mixture of twelve and of six syenites should have very nearly the same thorium content. It will be seen that the lower result agrees much better with the results obtained for other rocks in the group, and that it also gives a more normal value for the ratio of radium to thorium. It would thus appear that the lower value is the more probable one.

In order to see whether it was possible that the activity of a solution might go on steadily increasing with time, the following test was made. A solution containing ten grams of the 23 acid volcanic and intrusive mixture was made up on the 13th of April. This solution was tested on the 20th of April, and again about a fortnight later on the 6th of May. On both occasions it gave a result of 2.2×10^{-5}. This result would tend to show that the activity of a solution becomes constant after the first few days, as one would expect from the rates of decay of the various disintegration products involved. To further test the method, the manner of making up the solutions was varied, and the melt from a rock dissolved in its entirety directly in HCl, without being first treated with water. However, the 18 basalts when treated in this way gave nearly the same result as they had given before by the usual method. It was then thought that the limpidity of a solution might possibly affect the ease with which it parts with its emanation. Some of the solutions used in the above experiments were perfectly clear, but a few of them were cloudy owing to the presence of a certain amount of gelatinous silica. One might perhaps suppose that the emanation in the solution might be partially entrapped in the silica, and so that a cloudy solution would give a lower result than a clear solution. In connexion with this conjecture three solutions each containing five grams of Krakatoa ash were made. One of these solutions was made in the ordinary way, and the resulting solution was rather cloudy. In each of the other two cases two grams of $KClO_3$ were added to the fusion mixture. This addition seemed to have a very good effect, as the melt on solution gave a perfectly limpid solution. In one solution also the amount of HCl was increased to see if this would affect the result. It will be seen, however, that the three solutions gave practically the same value, indeed the differences are probably within the limits of experimental error for the method. Of the two, the cloudy solution gave the higher result. This may possibly be due to the fact that the presence of a small amount

of gelatinous silica may lead to better boiling of the solution. The amount of HCl used, too, seems to have little effect on the result, as the solutions made up with 50 c.c. and 100 c.c. of acid respectively gave nearly identical results. Thus from this series of trials it would appear that the exact method of treating the rock has not much effect on the final result, which is satisfactory.

It is rather difficult to arrive at a mean result for the thorium content from the values obtained. We can either simply take the mean of all the results obtained, or we can attach to each result a weight proportional to the number of rocks in the powder from which the result was obtained. The means obtained by both methods are given. A slightly higher result is obtained by the second method. This is due to the fact that there is a larger number of acid rocks in the powders than either intermediate or basic rocks. Of course by neither method can we hope to obtain the real mean value of the thorium content of the earth's crust. To do this, we should know its average composition, *i. e.* the percentage of acid, intermediate, and basic types in it. The amount of sedimentary rocks could probably be neglected without making much difference in the result. It is generally thought that the composition of the lithosphere approximates to that of a diorite or andesite, *i. e.* it is intermediate in chemical character. On this supposition the average thorium content would be about $1\cdot6 \times 10^{-5}$. This value is of course obtained only from surface materials, and we are not justified in assuming that the thorium content is not different at some distance below the surface. The mean for the acid rocks alone is $2\cdot08 \times 10^{-5}$ and for the basic rocks $0\cdot56 \times 10^{-5}$. These means are obtained by the second method. By the same method we obtain a general mean for the experiments of $1\cdot50 \times 10^{-5}$. In these results the miscellaneous rocks are neglected. The values are obtained from 86 acid, 48 intermediate, and 56 basic rocks. If we take the simple arithmetical means we obtain slightly different values, *i. e.* acid $2\cdot13$, intermediate $1\cdot50$, and basic $0\cdot51$. The corresponding general mean is $1\cdot38 \times 10^{-5}$.

In conclusion I wish to express my sincere thanks to Dr. Joly for his most kind aid and advice during the progress of the experiments.

Iveagh Geological Laboratory,
          December 1914.

LIII. *The Duplex Harmonograph.* *By* J. H. Vincent,
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Paddington Technical Institute*.

[Plate VIII.]

Contents.

INTRODUCTION.

THE pendulum harmonograph has been developed in various ways since its first introduction. By using a vertically vibrating stereoscopic camera to photograph the horizontal movement of the tracing point, pictures which, when combined, show harmonic motion in three dimensions have been obtained. The well-known twin-elliptic pendulum in the forms given to it by Goold and Benham † draws the resultant of four simple harmonic motions with the condition that they consist of two pairs of nearly equal frequency.

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* Communicated by the Authors.
† "Harmonic Vibrations," by Goold, Benham, Kerr, and Wilberforce. Newton and Co., London, n. d.

If one receives the traces of an ordinary harmonograph on a table at the top of an elliptic pendulum mounted on gimbals, after Benham, the elliptic vibration can be combined with the motion of the other pendulums. By the use of an electrolytic method of tracing, we have already shown how the sense and speed of the motion of the tracing-point can be recorded on harmonograms[*].

Harmonographs in general have the defect that the pictures, although entrancingly beautiful, require much skill on the part of the experimenter, combined with good fortune, for their production. In particular, the amplitudes and phases of the constituent vibrations have usually depended on the dexterity and luck of the operator. In the instrument which we shall now describe little is left upon which the experimenter can exercise his skill. When suitably adjusted the instrument will draw the same diagram with the regularity of a printing machine. The amplitudes and phases of the motion are under control, and the interference of the experimenter consists merely in placing the writing point on the prepared surface and removing it when the record has been traced.

Tisley's harmonograph draws the resultant of two simple harmonic motions at right angles to each other. The Duplex Harmonograph replaces each of these motions by the sum of two simple harmonic motions in the same straight line.

CONSTRUCTION OF THE APPARATUS.

In fig. 1, A, B, C, and D are knife-edges of four pendulums placed at the corners of a square drawn on the horizontal surface of a thick slate slab. A and C swing in the vertical plane through AC and B and D in the vertical plane through BD. Each pendulum consists of a steel rod 113 cm. long and 2·2 cm. in diameter. Knife-edges are placed 22 cm. from the top and swing in grooves cut in flat steel rings placed over holes in the slate slab at the corners of the 56 cm. square. A centimetre of needle is fixed vertically to the top of each pendulum and passes through a hole in a light wooden rod. The rods on A and B meet at right angles at c in the centre of the square, where they are pierced by a sewing-needle (forming a hinge) with its point downwards. The point of this needle draws the curves on a

[*] 'Knowledge,' Jan. 1912.

table moved* by the pendulums C and D.   The upper end of
this needle passes through a hole in a strut of thin metal

Fig. 1.
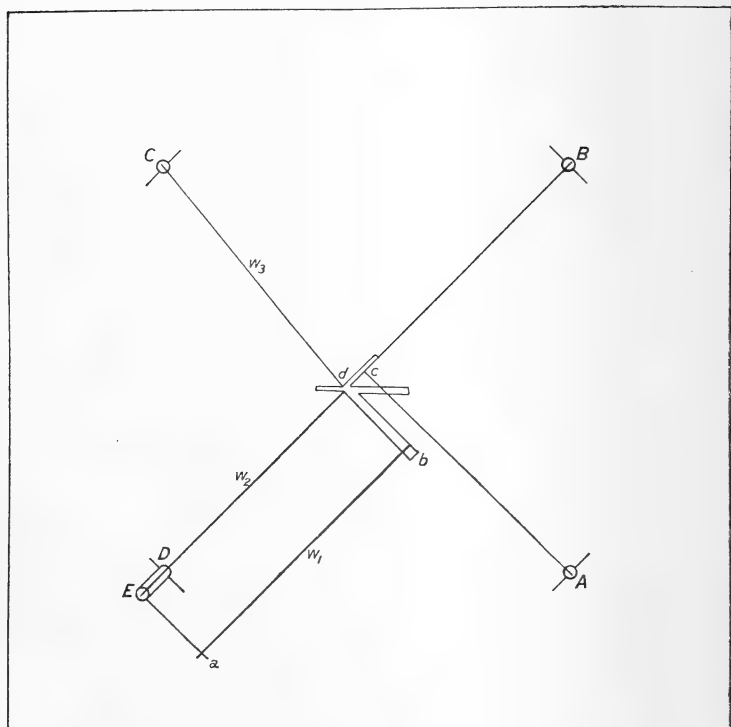
(not shown in the figures) rising from the lower of the two
rods A*c* and B*c*.   The rods from C and D are jointed at the

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* Curves of the character dealt with in this paper could be drawn on
a *fixed* table by the employment of other linkages, or by utilizing the
vibrations of coupled systems.   For example, let the pendulums situated
at opposite corners of the square be similar in all respects, and let each
pair be suitably coupled by light springs.   The pen is at the junction of
two light rods pivoted at the tops of two adjacent pendulums, its
position of rest being at the centre of the square.   The motion of any
pendulum is the sum of two simple harmonic motions whose frequencies
depend upon the free frequency of the pendulum and the strength of the
coupling.   The motion of the pen will therefore be the resultant of two
motions each approximately parallel to a diagonal of the square, each of
these motions being made up of the two simple harmonic motions proper
to the coupled system, to one pendulum of which the pen is attached.
If p^2 and ρ^2 be the accelerations per unit displacement along the x-dia-
gonal, due to gravity and relative displacement respectively, while

point d which lies vertically beneath the needle-point when all the pendulums are in their positions of rest. In the figure, pendulum D is shown with its bob displaced positively towards the centre of the square, while the other pendulums are in their positions of rest. The rod from D bears a light skeleton table which carries a standard lantern cover-glass $3\frac{1}{4}$ in. square, upon which the records are taken. In order to prevent the rotation of the table and consequent distortion of the picture, a line db in the frame of the table forms one side of a parallelogram whose other sides are the rod w_2, a steel rod Ea, 11 cm. long, fixed in the pendulum shaft, and a light wooden rod w_1 borne on a needle-point at a and pivoted with the table at b.

Fig. 2.
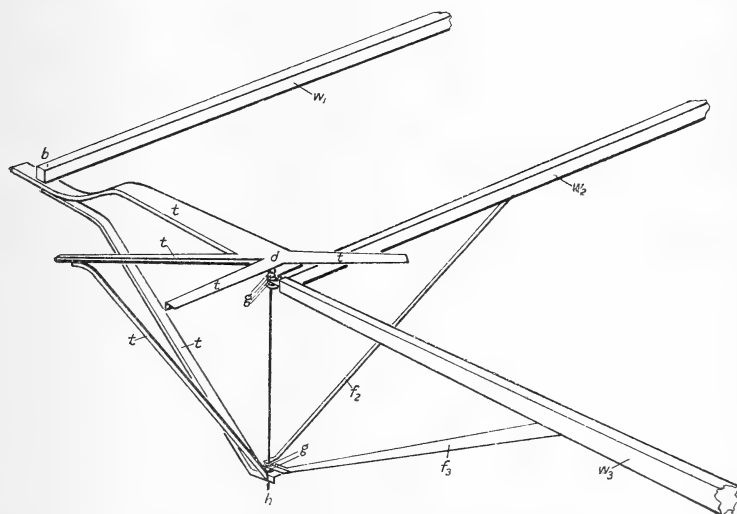
The details of the construction of the table are shown in fig. 2. This is a perspective sketch of the table as seen from the side BC of the slate slab. The skeleton table (t)

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q^2 and σ^2 refer to the y-diagonal, then the curves drawn will approximate to those having equations derived from

$$x = a \cos[pt+a] + c \cos[\sqrt{p^2+2\rho^2} \cdot t + \gamma]$$
$$y = b \cos[qt+\beta] + d \cos[\sqrt{q^2+2\sigma^2} \cdot t + \delta]$$

by eliminating t. The method here sketched is not practical, since the damping is large even when care is taken in designing the couplings. The method also lacks the flexibility in adjustment, which is a valuable feature in the duplex harmonograph described in the body of the paper.

is made of tinned sheet iron. The bases of the struts are soldered together and joined to the centre of the table by a large needle dh. This needle passes through holes at the ends of the wooden rods w_2 and w_3 which proceed from the tops of pendulums D and C respectively, and it also passes through holes in the bases of their tin struts f_2 and f_3. Excessive vertical play of these rods and struts on the needle is prevented by the use of glass beads g, which also serve to diminish friction.

If the pendulums at the ends of one of the sides of the square ABCD be clamped the others will draw an ordinary harmonogram or Lissajous' curve. In fig. 1 let x be the displacement towards A of the tracing-point from its position of rest, and y that towards B; the curves drawn by the instrument will approximate to those having equations derived from

$$\left. \begin{array}{l} x = a \cos \left[\, pt + \alpha \,\right] + c \cos \left[\, rt + \gamma \,\right] \\ y = b \cos \left[\, qt + \beta \,\right] + d \cos \left[\, st + \delta \,\right] \end{array} \right\} \quad \cdot \quad \cdot \quad (1)$$

by eliminating t. So that this apparatus is capable of drawing a class of curves bearing a relation to Lissajous' figures similar to that which epicyclics bear to circles.

Initial Amplitude and Phase.

A very important part of the apparatus is an iron bar of square section which is fixed vertically under the middle of the slate table with its flat surfaces at right angles to the diagonals of the square. Any pendulum can be held at rest with its bob displaced outwards (negatively) by means of a light wooden rod, provided with a screw which rests on the edge of a flat surface of the central iron bar. By altering the length of this rod by means of the screw, the amplitude can be accurately adjusted. A pendulum thus poised can be released at the instant when either of the pendulums adjacent to it has accomplished any desired part of its initial half-swing, by the impact of the end of a rod of adjustable length carried permanently by the releasing pendulum. This re-leasing rod can be either a plain straight rod for knocking off the propping bar, or one provided with a cross piece at the end to pull off this amplitude-bar.

When it is desired to release two or more of the pendulums simultaneously, electromagnets are employed. By these and similar means the initial amplitudes and relative phases

of the pendulums are under complete control. After having roughly adjusted the frequencies by timing with a stop-watch, the accurate timing is performed under the guidance of the simple harmonograms drawn by adjacent pairs. The accuracy of the releases and the adjustment of the amplitudes are similarly tested. The duplex harmonogram is then drawn and can be identically repeated at pleasure.

Friction.

The beauty of many of the pictures drawn by previous harmonographs is largely owing to the decrease of the amplitudes by friction and to slight defects in tuning. Our pendulum-bobs were very heavy, and the friction of the tracing-point was in some cases almost negligible. The smallness of the friction is largely owing to the suspension of the framed table, supporting the glass plate, from the roof of the laboratory by a light thread. This device, though theoretically inelegant, inasmuch as it introduces extra restoring forces, has in practice no detrimental effect.

DESCRIPTION OF THE DUPLEX HARMONOGRAMS.

The pictures were in the first place white line drawings on the smoked background. The plates show the drawings reversed, light for dark, prepared for the press by a photographic process in which the sensitive surface was facing in the same direction as the original trace. Figures 7 to 18 are reproduced full size, the others being reduced as seven to eight.

Unequal Frequencies in Simple Ratios; Friction Small.

The frictional damping is not sufficient to separate the successive paths of the tracing-point when the quantities p, q, r, and s in equation (1) are as small whole numbers. So that, unless friction is purposely introduced, the record has to be stopped when the complete path has been traced once. A few diagrams taken under the conditions that p, q, r, and s are as simple whole numbers and that friction is small will be described first.

Index of Diagrams 1 *to* 18.

No.	Frequencies as	Pendulums at rest.	Initial conditions (amplitudes all a).	
1	⎫	none	⎫	⎫
2	⎪	A	⎪	⎪
3	⎬ 2, 3, 4, 5	B	⎪	⎪
4	⎪	C	⎪	⎪
5	⎭	D	⎬ Displacements all negative.	⎪
6	⎫	none	⎪	⎪
7	⎪	B	⎪	⎬ All starting together.
8	⎪	C	⎪	⎪
9	⎪	D	⎭	⎪
10	⎪	none	⎫	⎪
11	⎪	B	⎬ All negative except A.	⎪
12	⎪	D	⎭	⎪
13	⎬ 1, 2, 3, 4	none	⎫	⎪
14	⎪	A	⎬ All negative except B.	⎪
15	⎪	C	⎭	⎪
16	⎪	none	A and B positive, C and D negative.	⎭
17	⎪	none	⎧ D releases C, C releases B. B releases A when each has completed a quarter of a vibration.	⎫ All start from negative position.
18	⎭	none	⎧ D releases B, B releases A and C at once as above.	⎬

Frequencies as 2, 3, 4, 5.

The frequencies are in the ratios 2, 3, 4, and 5, while the amplitudes are equal. All the bobs are started together from their outside position. For fig. 1, in which all four pendulums are swung, the equations to the trace become

$$x = a \cos [2pt + \pi] + a \cos [4pt + \pi],$$
$$y = a \cos [3pt + \pi] + a \cos [5pt + \pi].$$

In figs. 2, 3, 4, and 5 the pendulums A, B, C, and D respectively are at rest, so that the corresponding pairs of equations are derived from those of fig. 1 by deleting the appropriate term. In all five cases the record extends from $t = 0$ to $t = \pi/p$. The length of the record in time is the same in all the figures up to and including fig. 16.

Frequencies as 1, 2, 3, 4.

Initial displacements all negative.

Figs. 6 to 9 form a similar group of diagrams to that discussed in the previous paragraph, the frequencies being now proportional to the numbers 1, 2, 3, and 4, while pendulums B, C, and D are fixed in turn in each of the figures 7 to 9. The curves in each case represent one half the time required to complete a cycle of operations, the appropriate equations being derived from those of the previous paragraph by substituting 1, 2, 3, and 4 for 2, 3, 4, and 5. If pendulum A is clamped the other three draw a diagram identical with fig. 5 turned anti-clockwise through a right angle.

Various initial conditions.

The conditions are unaltered except that A is started from its extreme position of positive displacement.

The equations to the trace in fig. 10 are therefore

$$x = a \cos pt \qquad + a \cos [3pt + \pi],$$
$$y = a \cos [2pt + \pi] + a \cos [4pt + \pi].$$

Figs. 11 and 12 are drawn with pendulums B and D fixed in turn. The equations corresponding to these cases are found by deleting the first and second terms respectively in the expression for y.

In figs. 13, 14, and 15 the initial displacement of B is positive, while the other pendulums start with their bobs in the outer position. The amplitudes are equal and the pendulums are released simultaneously. The equations to the curve shown in fig. 13 are

$$x = a \cos [pt + \pi] + a \cos [3pt + \pi],$$
$$y = a \cos 2pt \qquad + a \cos [4pt + \pi].$$

The equations to the curves 14 and 15 are found by omitting in turn the first and second terms in the expression for x.

In fig. 16 pendulums A and B are started from the inside position, while C and D commence from the outside. The equations to the trace are thus

$$x = a \cos pt + a \cos [3pt + \pi],$$
$$y = a \cos 2pt + a \cos [4pt + \pi].$$

To draw fig. 17 we employ the methods described in the paragraph headed " Initial Amplitude and Phase " to control the circumstances of release. The amplitudes and periods

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of the pendulums are unchanged. A, B, and C are supported in their negative positions by props adjusted to give equal initial amplitudes. D is released from a corresponding position and is provided with a wooden arm to remove the amplitude-rod supporting C when D is passing through its position of rest ; C in like manner releases B, which in turn liberates A. Thus the rods of all the pendulums except A carry releasing rods attached to them, which involves the re-adjustment of the periods. If we measure time from the instant when the pendulum A is released, the equations to the trace are

$$x = a \cos\left[pt + \pi\right] \qquad\qquad + a \cos\left[3p(t + \pi/6p + \pi/4p) + \pi\right],$$
$$y = a \cos\left[2p(t + \pi/4p) + \pi\right] + a \cos\left[4p(t + \pi/8p + \pi/6p + \pi/4p) + \pi\right],$$

the record enduring in this case from $t = 0$ to $t = 2\pi/p$.

By employing a small wooden triangle pivoted near one corner to change the direction of motion due to the impact of a releasing rod through 90° (after the manner of a bell-crank lever) it was arranged in fig. 18 that D should at the middle of its swing release the opposite pendulum B. The pendulum B in its mid-swing releases A and C simultaneously. If we count time from this instant the equations to the trace become

$$x = a \cos\left[pt + \pi\right] \qquad\qquad + a \cos\left[3pt + \pi\right],$$
$$y = a \cos\left[2p(t + \pi/4p) + \pi\right] + a \cos\left[4p(t + \pi/4p + \pi/8p) + \pi\right].$$

The time occupied in the trace is, as in the preceding picture, $2\pi/p$.

Epicyclics, &c.

If two adjacent pendulums having the same frequency and amplitude form one pair, while the other pair are also equal to each other in these respects, we can draw epicyclics by releasing one pendulum of each pair a quarter of its period later than the other.

Friction Small.

Figures 19 to 30 include examples of well-known epicyclics. To draw these figures, A was tuned in unison with B, and C with D. All four pendulums were initially supported with their bobs in the outward position. If B liberates A a quarter of a period after its own release, the pen is given a uniform clockwise circular motion. If D similarly releases C, the table describes circles in the same sense. The motion

Index of Diagrams 19 to 35.

No.	Frequency Ratio. A & B	C & D	Initial Amplitudes. A & B	C & D	Class, direct or retrograde.	Nature of Roulette.	Remarks.
19	1	3	a	a	direct	epitrochoid	.
20	1	3	a	a	retrograde	hypotrochoid	
21	1	3	a	$a/3$	direct	epicycloid	Well-known caustic by reflexion.
22	1	3	a	$a/3$	retrograde	hypocycloid	Astroid.
23	1	2	a	a	direct	epitrochoid	Trisectrix.
24	1	2	a	a	retrograde	hypotrochoid	
25	1	2	a	$a/2$	direct	epicycloid	Cardioide.
26	1	2	a	$a/2$	retrograde	hypocycloid	Tri-cusp.
27 and 28	p	$p+h$	a	a	retrograde	hypotrochoid	Path of electron vibrating in magnetic field.
29	p	$p+h$	a	a (D fixed)	not an epicyclic.	not a roulette.	
30	p	$p+h$	a	a	direct	epitrochoid	
31	p	$p+h$	$a(p+h)/p$	a	retrograde.	hypocycloid	
32	...	...	A & B fixed	a	not an epicyclic.	not a roulette.	Involute of a circle.
33	2	1	$a/3$	a	direct	family of epitrochoids	Limaçon of Pascal... cardioide...trisectrix.
34	2	1	$a/3$	a (D fixed)	not an epicylic.	not a roulette.	
35	2	1	$a/3$ (B fixed).	a	not an epicyclic.	not a roulette.	

of the pen relatively to the table is thus compounded of two uniform circular motions in the same direction. The trace will be a direct epicyclic, the two motions being sometimes spoken of as "concurrent." If the pendulum C releases D the trace is a retrograde epicyclic due to the combination of "countercurrent" circular motions. The direct epicyclics are all epi-trochoids or epi-cycloids, while the retrograde epicyclics are hypo-trochoids or hypo-cycloids.

Frequencies in simple ratio.

In figure 19 all the amplitudes are equal. The frequency of the pendulums C and D is three times that of pendulums

A and B.   The circular motions are both clockwise.   The trace is the epitrochoid drawn by a point at a distance a from the centre of a circle of radius $a/3$ rolling on a fixed circle of radius $2a/3$.   In drawing such curves, one pair of pendulums having been suitably released, the other pair was started at a time most convenient to the experimenter, so that the orientation of the diagram in such figures is not determinate.   Further, the commencement of the drawing was also arbitrary since we put the pen down so as to prevent the overlap interfering with an interesting portion of the trace.   If, then, we insert θ and ϕ in the corresponding pairs of terms, the equations to the trace may be written

$$x = a \cos [pt + \theta] \qquad\qquad + a \cos [3pt + \phi],$$
$$y = a \cos [p(t + \pi/2p) + \theta] + a \cos [3p(t + \pi/6p) + \phi].$$

In figs. 19 to 26 the duration of the trace is the period of the slower pair of pendulums.

All else being unchanged, the circle drawn by C and D is reversed in fig. 20.   The trace is the hypotrochoid described by a point distant a from the centre of a circle of radius $a/3$ which rolls inside a fixed circle of radius $4a/3$. The equations to the trace are

$$x = a \cos [pt + \theta] \qquad\qquad + a \cos [3p(t + \pi/6p) + \phi],$$
$$y = a \cos [p(t + \pi/2p) + \theta] + a \cos [3pt + \phi].$$

Owing to unequal damping, the curves in figs. 19 and 20 did not pass through the origin of coordinates as they would have done had the conditions been ideal.

If, now, the amplitudes are made inversely as the frequencies, fig. 19 will become fig. 21, while fig. 20 is replaced by fig. 22.   The equations to fig. 21 may be written

$$x = a \cos [pt + \theta] \qquad\qquad + a/3 \cos [3pt + \phi].$$
$$y = a \cos [p(t + \pi/2p) + \theta)] + a/3 \cos [3p(t + \pi/6p) + \phi].$$

This is the well-known caustic by reflexion of parallel rays from the inside of a circle of radius $4a/3$.   It is the epicycloid due to the rolling of a circle of radius $a/3$ on a circle of twice its radius.

The equations to fig. 22 are

$$x = a \cos [pt + \theta] \qquad\qquad + a/3 \cos [3p(t + \pi/6p) + \phi].$$
$$y = a \cos [p(t + \pi/2p) + \theta] + a/3 \cos [3pt + \phi].$$

The curve is a four-cusped hypocycloid, or astroid, traced by a point on the circumference of a circle of radius $a/3$ rolling inside a circle whose radius is $4a/3$.

Epicyclic curves may be drawn with a definite orientation if we provide a method of fixing the initial positions of the radius vectors of the circular motions. Thus the astroid could be drawn with its cusps on the axes of coordinates by providing B with two rods so as to release C and A simultaneously, as was done in fig. 18, C then similarly releasing D. Counting time from the instant when C and A are released, the equations to the trace would be

$$x = a \cos [pt + \pi] \qquad\qquad + a/3 \cos [3pt + \pi],$$
$$y = a \cos [p(t + \pi/2p) + \pi] + a/3 \cos [3p(t - \pi/6p) + \pi].$$

or
$$x^{2/3} + y^{2/3} = (4a/3)^{2/3}.$$

Since the evolute of an ellipse may be derived from the astroid by homogeneous strain, to draw the evolute of the specified ellipse

$$x^2/a_1^2 + y^2/b_1^2 = 1,$$

we must make the amplitudes of A and C equal to

$$3(a_1^2 - b_1^2)/4a_1 \quad \text{and} \quad (a_1^2 - b_1^2)/4a_1 \text{ respectively,}$$

and those of B and D equal to

$$3(a_1^2 - b_1^2)/4b_1 \quad \text{and} \quad (a_1^2 - b_1^2)/4b_1 \text{ respectively,}$$

while the method of release and the frequencies of vibration are unchanged.

Figs. 23 and 24 are drawn with the amplitudes equal, the ratio of the frequencies of the pairs of pendulums being 1 to 2 ; fig. 23 is the direct and 24 the retrograde epicyclic. The equations to fig. 23, in which the circles are both anti-clockwise, are

$$x = a \cos [p(t + \pi/2p) + \theta] + a \cos [2p(t + \pi/4p) + \phi],$$
$$y = a \cos [pt + \theta] \qquad\qquad + a \cos [2pt + \phi].$$

This curve is the trisectrix, the epitrochoid traced by a point distant a from the centre of a circle of radius $a/2$ rolling on a circle of equal radius. The equations to fig. 24 are

$$x = a \cos [pt + \theta] \qquad\qquad + a \cos [2p(t + \pi/4p) + \phi],$$
$$y = a \cos [p(t + \pi/2p) + \theta] + a \cos [2pt + \phi].$$

This hypotrochoid is described by a point distant a from the centre of a circle of radius $a/2$ rolling inside another circle of radius $3a/2$.

Figs. 25 and 26 are related to figs. 23 and 24 like figs. 21 and 22 are related to figs. 19 and 20. In fig. 25 the amplitudes of the motions of A and B are twice those of C and D,

the two direct circular motions having radii inversely as their frequencies. The equations to fig. 25 are

$$x = a \cos \left[p(t + \pi/2p) + \theta \right] + a/2 \cos \left[2p(t + \pi/4p) + \phi \right],$$
$$y = a \cos \left[pt + \theta \right] \qquad\qquad + a/2 \cos \left[2pt + \phi \right].$$

The origin of coordinates was marked by the needle on the prepared plate with the pendulums at rest. This curve is the cardioide, the epicycloid traced by a point on the circumference of a circle of radius $a/2$ rolling on an equal circle.

To draw fig. 26 one of the component circular motions of fig. 25 must be reversed. The equations to the trace are

$$x = a \cos \left[pt + \theta \right] \qquad\qquad + a/2 \cos \left[2p(t + \pi/4p) + \phi \right],$$
$$y = a \cos \left[p(t + \pi/2p) + \theta \right] + a/2 \cos \left[2pt + \phi \right].$$

The curve is the tri-cusp, the three-cusped hypocycloid drawn by a point on the circumference of a circle of radius $a/2$ rolling inside a circle of radius $3a/2$.

Frequencies slightly different.

In the foregoing examples of epicyclics the frequencies have been in simple ratio. If this ratio is slightly departed from the whole trace may be regarded as a family of curves, each member of which approximates to that proper to the simple ratio, while each successive member is rotated about the origin. The only examples of this character which we shall give have the ratio of the frequencies nearly unity.

In figs. 27 and 28 the frequencies of the first pair A and B are slightly less than those of C and D. The amplitudes are equal. The anti-clockwise circular motion due to C and D has slightly greater angular velocity than the clockwise motion. The equations to the trace are

$$x = a \cos \left[pt + \theta \right] \qquad\qquad + a \cos \left[\{ p + h \} (t + \pi/2\{ p + h \}) + \phi \right],$$
$$y = a \cos \left[p(t + \pi/2p) + \theta \right] + a \cos \left[\{ p + h \} t + \phi \right],$$

in which h is small compared with p. The trace lasts for a time $2\pi/h$ in fig. 27 and π/h in fig. 28. The curve is the hypotrochoid traced by a point distant a from the centre of a circle of radius $ap/\{ p + h \}$ rolling inside a fixed circle of radius $a\{ 2p + h \}/\{ p + h \}$.

"This is intimately connected with the explanation of two sets of important phenomena,—the rotation of the plane of polarization of light, by quartz and certain fluids on the one hand, and by transparent bodies under magnetic forces on the other . . . . . It will also appear in kinetics as the path

of a pendulum-bob which contains a gyroscope in rapid rotation *."

Our apparatus was originally set up in order to illustrate the vibration of a vibrating electron in a magnetic field †. If we regard the radiation of energy from the vibrating electron as a continuous process, the loss of amplitude is roughly illustrated by the inevitable frictional decrement.

Fig. 29 results from the suppression of one of the constituents of the motion. The equations to the trace are obtained from those to fig. 27 by omitting the second term in the expression for y. We may regard the motion as being elliptical at any instant, the family of ellipses having the origin as the common centre. The two straight lines $y^2 = a^2$, and the two circles $(x^2 + y^2)^2 = 4a^2 x^2$ constitute the complete envelope of the family. The pen remained down during the same period as in drawing fig. 27.

Fig. 30 corresponds with fig. 27, but now the component circular motions are in the same direction. In this instance, the pen was placed on the table when the pendulums D and B were released. The simultaneous start of C and A thus occurs when the pen is at $(-2a, 0)$. The trace is at first distorted by the vibrations of the pendulum-rods thus set up. The tuning of the pendulums was that employed in fig. 27. The equations to the trace drawn by the four pendulums may in this case be written in the more definite form

$$x = a \cos [pt + \pi] \qquad\qquad + a \cos [\{p + h\}t + \pi],$$
$$y = a \cos [p(t + \pi/2p) + \pi] + a \cos [\{p + h\}(t + \pi/2\{p + h\}) + \pi],$$

where t is counted from the release of C and A, the record lasting slightly longer than π/h. The innermost loop of the curve is distorted by the backlash due to the play of the jointed parts. The trace is a portion of an epitrochoid traced by a point distant a from the centre of a circle of radius $ap/\{p + h\}$ rolling outside a circle of radius $ah/\{p + h\}$.

Fig. 31 is similar to fig. 27, but now the amplitudes are inversely as the frequencies. The equations to the trace are

$$x = a\{p + h\}/p \cos [pt + \theta] \qquad\qquad + a \cos[\{p + h\}(t + \pi/2\{p + h\}) + \phi],$$
$$y = a\{p + h\}/p \cos [p(t + \pi/2p) + \theta] + a \cos[\{p + h\}t + \phi].$$

In this case the duration of drawing is $2\pi/h$. The curve is the hypocycloid due to the rolling of a circle of radius a inside a circle of radius $\{2p + h\}a/p$. The small blank area at the centre of the figure should have been sensibly circular and of radius ha/p.

* Thomson and Tait, ' Natural Philosophy,' Part I.
† Wood, ' Physical Optics,' 1911, p. 506.

Frequencies in Simple Ratio but Unequally Damped.

The design of the table allows of an adjustment in the friction which enables one to damp unequally the motion of the table and the tracing-point. For instance, let the tracing-point and the attaching rods be kept as light as possible, while the table is released from its suspending thread, loaded, and supported on an oiled glass plate by the lower end h (fig. 2) of its axial needle. The damping of the motion of the table can be made as large as is wished with respect to the damping of the tracing-point by adjusting the load.

If one pair of pendulums is clamped, say those bearing the tracing-point, and the other two set to draw a circle, when the tuning is accurately adjusted, and the friction small as before, the needle-point does not draw a recognizable spiral, but clears the smoke away from an annular surface. If, however, the motion of the table be sensibly damped we get fig. 32.

The chief feature of this curve is the regularity of the spacing of the successive branches. The original was measured in a random direction through the centre on a travelling microscope, and it was found that the distance between the branches was, as nearly as could be measured, ·100 cm. No change in the distance could be detected until one approached within a single turn of the point of rest. The friction was in this case almost entirely due to that of the axial needle in contact with the oiled glass plate. This suggests that the trace is the orbit of a point moving with an acceleration towards a fixed centre varying directly as the distance, under a constant frictional resistance. A solution to this dynamical problem is that the orbit may be the involute of a circle of radius l, the acceleration towards the centre being k times the distance from the centre, and the retardation being $2\,lk$. On this view, the circle of which the trace is the involute has a radius of ·016 cm., so that if we regard the friction as being strictly independent of the velocity, the tracing-point will come to rest ·016 cm. away from the frictionless position of equilibrium. The motion departs from one of uniform angular velocity about the centre of force by a term involving merely the square of the ratio of l to r, so that the tracing-point moves with sensibly uniform angular velocity until it closely approaches the end of its path.

Fig. 33. If two direct circular motions are compounded, whose frequencies are in the ratio 1:2, the curve drawn is the limaçon of Pascal, cardioide, or trisectrix, according as their amplitudes are in the ratios 3 : 1, 2 : 1, or 1 : 1 respectively,

the circle of higher frequency having the smaller amplitude.
If pendulums C and D are set to draw the involute as in
fig. 32, while A and B draw a circle in the same direction
whose radius is as nearly unaffected by friction as is practi-
cable, we may by arranging that the initial radii are as 3:1
draw a curve approximating very closely to the limaçon of
Pascal. As the ratio of the radii sinks in value owing to the
damping of the motions of pendulums C and D, a stage is
reached when the shrinking radius is twice that of the circle,
and the cardioide is described. Passing through this stage,
the decrease in the radius of the slower motion progresses
until the radii become equal, which transforms the trace into
a trisectrix. The needle was then removed from the plate,
and when all had been reduced to rest a mark was made on
the prepared surface by the tracing point. This black speck
should be visible in the diagram on the trisectrix at the
inner vertex of its loop, but in our picture it is very slightly
displaced within the loop. The apses lie on a straight line
through the centre. This confirms the view that the motion
of the damped pendulums is isochronous through the range
covered in the picture.

The arrangements for fig. 34 are as for fig. 33, except that
D is fixed, so that the trace is drawn by a point with a uni-
form circular motion of slowly diminishing amplitude to-
gether with a simple harmonic motion which is rapidly
damped. The frequency of the motion in the circle is twice
that of the single vibration. The initial amplitude of the
single vibration is three times the radius of the circle. The
style was removed when the slower vibration had almost died
away, leaving the circular motion alone operative.

In fig. 35, we have the involute of the circle as in fig. 32
combined with a simple harmonic motion due to the vibration
of pendulum A, B being clamped. The needle was removed
when the damped pendulums C and D, drawing the involute,
had come to rest.

Three Frequencies : Two Opposite Pendulums
beating.

The Duplex Harmonograph lends itself readily to the
description of figures in which the combined rectilinear
motions are themselves subject to periodic change in
amplitude after the manner of beats in acoustics. Of this
kind of diagram we shall give a few examples divided into
four classes. In the first three of these classes we shall deal
only with three frequencies. In the first, the mean frequency

of the beating pendulums is equal to the frequency of the
motion at right angles. In the second, the mean frequency
is twice that of the third frequency, while in the third class
the mean frequency is half that of the remaining frequency.
The fourth class will contain examples involving four
frequencies such that simple relations hold between the
means of the frequencies of oppositely-placed pendulums.

Index of Diagrams 36 to 46.

No.	Frequencies of beating pendulums as	Mean freq. of beating pendulums.	Other frequency.	Pendulums recording.	Initial Conditions.
36	$p+h$ and $p-h$	p	p	All recording except B in No. 37.	D releases C. B releases A. Displacements all negative except pendulum C in No. 42.
37					
38					
39					
40	$2p+h$ and $2p+3h$	$2p+2h$	$p+h$		All starting together.
41					
42					
43	$p+h$ and p	$\dfrac{2p+h}{2}$	$2p+h$		C releases D. A releases B.
44					
45					
46					

The other Frequency their Mean.

In fig. 36 pendulums B and D are tuned in unison, while
A and C have frequencies respectively greater and smaller
by equal amounts. B and D release A and C as they pass
through their mean positions. All four amplitudes are
initially equal. In this case we have allowed the pen to be
in contact with the prepared surface from the commence-
ment of the motion of the pendulums B and D. The tracing-
needle begins by drawing a circle of radius $2a$ and is removed
when it has traced the approximate straight line along y.
If friction had been completely eliminated the length of this
line would have been $4a$. Counting time from the simul-
taneous release of A and C, the equations to the trace are

$$x = a \cos \left[\{ p+h \} t + \pi \right] \qquad + a \cos \left[\{ p-h \} t + \pi \right],$$
$$y = a \cos \left[p(t + \pi/2p) + \pi \right] \quad + a \cos \left[p(t + \pi/2p) + \pi \right],$$

the record extending to $t = \pi/2h$. The displacement along x

being $2a \cos ht \cos [pt + \pi]$, the instantaneous value of the amplitude may be regarded as $2a \cos ht$, whilst the oscillations are always in quadrature with the motion along y. The trace is the projection of the motion of a point in a circle of radius $2a$ with uniform angular velocity p, the circle rotating about a diameter with uniform angular velocity h. Similar methods of representation are applicable in other cases. Frictional decrement can likewise be represented on this view.

Fig. 37 was produced under identical conditions with the exception that the motion of B was suppressed. It may be regarded as the projection of fig. 36 on a plane at 60° to it through the axis of x.

Fig. 38 is produced by altering the conditions of release from those of fig. 36. The bobs of all the pendulums start from their outward positions simultaneously. The equations to the trace are

$$x = a \cos [\{p+h\}t + \pi] + a \cos [\{p-h\}t + \pi],$$
$$y = a \cos [pt + \pi] \qquad + a \cos [pt + \pi],$$

so that the displacements along x and y pass through their zero values simultaneously. The trace lasts from $t = \pi/h$ to $t = 2\pi/h$. In this time the amplitude of the approximately rectilinear simple harmonic motion changes from its maximum value $2\sqrt{2}a$, passes through its minimum $2a$, and again attains its maximum. During this interval the direction of the resultant motion changes through a right angle, and when $t = 2\pi/h$ the motion is again at 45° to the axes. The amplitude of the motion along the axis of x now begins to decrease, and the direction of the resultant rectilinear vibration rotates in the opposite direction. This is illustrated in fig. 39, in which the oscillation of the direction of the resultant vibration can be readily traced owing to the loss of amplitude by friction as the oscillation takes place. The equations to the trace being as before, the record in fig. 39 lasts for the time $2\pi/h$ from $t = \pi/2h$. If friction had been inoperative both diagrams would have been bounded by $y = \pm 2a$.

The other Frequency half their Mean.

The pendulums are now tuned so that the third frequency is half that of the mean frequency of the pair of oppositely-placed pendulums which produce beats together.

In fig. 40 the frequencies are in the ratios $2p + h$, $p + h$, $2p + 3h$, $p + h$. All the amplitudes are equal, and the pendulums are released together from their extreme outer

positions.   The needle is allowed to trace from the com-
mencement of motion during half the cycle of operations, so
that the equations to the trace are

$$x = a \cos \left[\{2p+h\}t + \pi \right] + a \cos \left[\{2p+3h\}t + \pi \right],$$
$$y = a \cos \left[\{p+h\}t + \pi \right] \; + a \cos \left[\{p+h\}t + \pi \right],$$

from $t=0$ to $t=\pi/h$.   The trace commences with the
parabola $y^2 + ax - 2a^2 = 0$, and if we neglect the effects of
friction all the succeeding parabolas may be derived from
this by altering the scale of drawing and the sign of the
x-coordinate.   The points where all the parabolas cross the
axis of y are $(0, \pm a\sqrt{2})$, coinciding with the cusps of the
envelope of fig. 54.   Since the vibration along the axis of y
has a sensibly constant amplitude, the figures will be bounded
by the lines $y = \pm 2a$ and the parabolas $y^2 \pm ax - 2a^2 = 0$.

In the introduction we state that the figures may be re-
produced with fidelity.   This extends even to cases in which
the length of record varies, as the frictional loss is almost
the same whether the needle is in contact with the smoked
glass or not.   This is illustrated in fig. 41, in which the
second quarter of the complete cycle of operations is
shown.

In fig. 42 we are again only concerned with three different
frequencies, these being identical with those of figs. 40
and 41.   Pendulum C was in this case released with its bob at
the extreme inside position, all the other initial displacements
being negative.   On release the motion consists of a sensibly
rectilinear simple harmonic motion along the axis of y.   This
changes into motion in Lissajous' figure of eight.   The style
was placed down when the amplitude along the axis of x had
first attained its maximum.   The equations to the trace are

$$x = a \cos \left[\{2p+h\}t + \pi \right] + a \cos \{2p+3h\}t,$$
$$y = a \cos \left[\{p+h\}t + \pi \right] \; + a \cos \left[\{p+h\}t + \pi \right],$$

from $t = \pi/2h$ to $t = \pi/h$.

The other Frequency twice their Mean.

The remaining examples we shall give involving three
frequencies have the third frequency twice the mean of those
of the oppositely-placed beating pendulums.

In fig. 43 the frequencies are in the ratios $2p+h$, $p+h$,
$2p+h$, p.   The amplitudes are equal, and the pendulums
start together with their bobs displaced outwards.   The pen

traces during a quarter of a complete cycle. The equations to the trace are

$$x = a \cos \left[\{2p+h\}t + \pi\right] + a \cos \left[\{2p+h\}t + \pi\right],$$

$$y = a \cos \left[\{p+h\}t + \pi\right] + a \cos \left[pt + \pi\right],$$

from $t = 2\pi/h$ to $t = 3\pi/h$. On release, the motion is along the parabola with the maximum parameter. The component of this motion along the axis of y dies down to zero and then increases to a maximum, when the original parabola is again traced. At this stage, the pen was permitted to record and the trace was stopped when the motion had again become sensibly rectilinear.

We have had an example in fig. 42 in which motion in a Lissajous' figure of eight degenerates into rectilinear motion along one of its axes of symmetry. In fig. 44, the motion becomes rectilinear along the other axis of symmetry. The initial amplitudes of the four pendulums are equal while the frequencies again fulfil the conditions of fig. 43, but h is much smaller compared with p, so that the effect of the frictional decrement in the amplitude of the motion along x is very marked. A and C release B and D in mid-swing, the bobs all starting from their outer positions. Counting time from the instant when B and D commence to swing, the equations to the trace are

$$x = a \cos \left[\{2p+h\}t + 3\pi/2\right] + a \cos \left[\{2p+h\}t + 3\pi/2\right],$$

$$y = a \cos \left[\{p+h\}t + \pi\right] + a \cos \left[pt + \pi\right],$$

in which the frictional decrement is neglected. The record lasts until $t = \pi/h$. Instead of the figure being bounded by the two straight lines $x = \pm 2a$ its central portions are sensibly contracted, so that when the motion is reduced to oscillation along x its amplitude is no longer $2a$.

If the trace had been continued, this straight line would have opened out again into the figure of eight. This is shown in fig. 45, in which the trace commences when $t = \pi/h$. A corresponding frictional effect is again evident. The record again lasts for the time π/h. In fig. 46 a similar cycle of events is recorded, the pendulums having been slightly readjusted. In this case both the waning and the waxing in the y-direction are recorded, the time occupied being $2\pi/h$.

Four Frequencies; Pairs of Opposite Pendulums
beating.

We will now give a few examples from what we have called the fourth class of those figures in which oppositely-placed pendulums are beating.   In this class four frequencies are involved, simple relations subsisting between the means of the frequencies of opposite pendulums.

Index of Diagrams 47 *to* 54.

No.	Freq. of A & C.	Mean freq. of A & C.	Diff. of A & C.	Freq. of B & D.	Mean freq. of B & D.	Diff. of B & D.	Initial Conditions.
α. $\begin{cases} 47 \\ 48 \end{cases}$	$2p$ and $2p+2h$	$2p+h$	$2h$	p and $p+h$	$\dfrac{2p+h}{2}$	h	All negative. $\Big\}$ $\begin{cases} \text{A \& B negative} \\ \text{C \& D positive} \end{cases}$
β. 49	$p+h$ and $p-h$	p	$2h$	$p+2h$ and $p-2h$	p	$4h$	$\begin{cases} \text{A \& B negative} \\ \text{O \& D positive} \end{cases}$ All starting together.
γ $\begin{cases} 50 \\ 51 \\ 52 \\ 53 \\ 54 \end{cases}$	$2p+h$ and $2p+3h$	$2p+2h$	$2h$	$p+2h$ and p	$p+h$	$2h$	$\begin{cases} \text{A \& B negative} \\ \text{C \& D positive} \end{cases}$ $\begin{cases} \text{All negative} \\ \text{but C.} \end{cases}$ All negative. All negative. $\begin{cases} \text{All negative but D.} \\ \text{B releases C, D releases A.} \end{cases}$

α. *Mean frequencies and differences of frequencies of opposite pendulums as two to one.*

To satisfy these conditions the ratio of the frequencies will be $2p$, p, $2p+2h$, $p+h$. These frequencies are employed in figs. 47 and 48.   The initial amplitudes in both cases were equal.   In fig. 47 the pendulums were started with their bobs in the extreme outward position.   The tracing-point was put down on the plate when the bobs of the pendulums B and D had first reached their inward positions, so that counting time from this instant the equations to the trace are

$$x = a \cos \left[2pt + \pi\right] + a \cos \{2p+2h\}t + \pi],$$
$$y = a \cos pt \qquad + a \cos \{p+h\}t,$$

the trace lasting until $t = \pi/h$. In this figure h is again so small with respect to p that the effects of friction are noticeable.   Disregarding these effects, however, the excursions in the approximate parabolic path are limited by the initial

parabola $y^2 + ax - 2a^2 = 0$. At the beginning of the trace the
component rectilinear excursions along the axes diminish,
but the motion in the x-direction dies down more rapidly,
and when it is zero its amplitude changes sign so that the
subsequently growing parabolas turn their concavities in
the opposite direction. The trace continues until the para-
bolic motion has dwindled to an oscillation along the axis
of x.

Instead of releasing the pendulums so as to draw parabolas,
in fig. 48 they are started so that the successive curves are
all examples of Lissajous' figure of eight. The pendulums
are released simultaneously, A and B from their outward
positions and C and D from their inward positions. As the
quivering of the pendulum rods again proved troublesome,
the style was placed on the prepared surface when its motion
was approximately rectilinear along the axis of y. The
equations to the curve are

$$x = a \cos\left[2pt + \pi\right] + a \cos\{2p + 2h\}t,$$
$$y = a \cos\left[pt + \pi\right] + a \cos\{p + h\}t,$$

the trace lasting from $t = \pi/h$ to $t = 2\pi/h$. While the motion
along the axis of y decreases in amplitude, the motion along
the axis of x increases. This motion attains a maximum,
and then both begin to die away together and reach zero
value simultaneously, when the needle was removed from
the plate. By the time that the combined vibration along x
had reached its maximum amplitude, frictional damping had
notably affected its amount. Otherwise the whole figure
would have been enclosed in the space bounded by the four
parabolas

$$(y \pm a)^2 \pm ax/2 - a^2 = 0,$$

which also constitute the complete envelope.

β. *Mean frequencies equal and differences as in α.*

In this case the frequencies will be $p + h$, $p + 2h$, $p - h$,
$p - 2h$. In fig. 49, using these frequencies, with initial
amplitudes equal, pendulums A and B are released from their
extreme negative position, while C and D start with them
from the corresponding positive position. The equations to
the consequent trace are

$$x = a \cos\left[\{p + h\}t + \pi\right] + a \cos\{p - h\}t,$$
$$y = a \cos\left[\{p + 2h\}t + \pi\right] + a \cos\{p - 2h\}t,$$

the record extending from $t = \pi/h$ to $t = 2\pi/h$. The motion

at any instant may be regarded as approximately a simple harmonic motion in a straight line. The direction of vibration in this line oscillates through an angle $2 \tan^{-1} 2$; when $t = \pi/h$ the resultant amplitude is zero and its direction makes an angle $\tan^{-1}(-2)$ with the positive direction of the axis of x. This angle increases until, when the motion along y is zero (*i. e.* when $t = 3\pi/2h$) the maximum amplitude in the direction of x equals $2a$. In its growth from zero the amplitude passes through a maximum value of $5a/2$ when its direction of motion makes an angle $\tan^{-1}(-\sqrt{3/2})$ with the axis of x. If we neglect the decrement in the oscillations due to friction the excursions of the tracing-point are limited by the Lissajous' figure of eight

$$\begin{cases} x = 2a \sin ht, \\ y = 2a \sin 2ht, \end{cases}$$

or

$$x^2 - 4a^2 x^2 - 4a^2 y^2 = 0.$$

γ. *Mean frequencies as two to one and differences equal.*

The remaining examples of figures drawn by four pendulums in which the opposite pendulums are beating, all obey the conditions that the mean frequencies of the opposite pairs are as two to one and that the differences are equal, so that the frequencies may be taken proportional to $2p + h$, $p + 2h$, $2p + 3h$, p. Using three frequencies only, we have shown how families of Lissajous' figures of eight may be drawn in which succeeding members increase or decrease in one dimension, the curves in figs 44 and 42 degenerating into two straight lines respectively at right angles. In fig. 50 both these effects go on simultaneously and at the same rate. To draw the figure the pendulums were started together from positions of equal displacement, A and B outward and C and D inward. The needle was put down when the combined amplitudes were at a maximum, the record extending from $t = \pi/2h$ to $t = \pi/h$, the equations to the trace being

$$x = a \cos\left[\{2p + h\}t + \pi\right] + a \cos\{2p + 3h\}t,$$

$$y = a \cos\left[\{p + 2h\}t + \pi\right] + a \cos pt.$$

The complete trace would contain two families of similar and similarly-placed curves, each family consisting of two series in which the curves are increasing and decreasing respectively in amplitude, the curves in each family being described in contrary directions.

In fig. 50 the combined oscillations of the oppositely-placed pendulums are always in the same phase, while in fig. 51 they are always in quadrature. The bob of pendulum C was started from its inward position when the others were released from their outward positions. A and C are thus in opposition, while B and D conspire. The equations to the trace are

$$x = a \cos\left[\{2p+h\}t + \pi\right] + a \cos\{2p+3h\}t,$$
$$y = a \cos\left[\{v+2h\}t + \pi\right] + a \cos\left[pt + \pi\right],$$

from $t = \pi/2h$ to $t = \pi/h$. In this case the successive curves are still Lissajous' figures of eight. The process of passing from a straight line to another at right angles by transformation of the shape of the curve occupies the time $\pi/2h$. All the curves lie within the area enclosed by the parabolas

$$y^2 \pm 2ax - 4a^2 = 0,$$

which constitute the envelope.

Returning again to the condition that the resultant vibrations along the two axes shall be in the same phase, in fig. 52 we set these resultant motions to draw a parabola instead of a Lissajous' figure of eight, as in fig. 50. To do this the initial amplitudes of the two combined motions are maxima, the equations to the trace being

$$x = a \cos\left[\{2p+h\}t + \pi\right] + a \cos\left[\{2p+3h\}t + \pi\right],$$
$$y = a \cos\left[\{p+2h\}t + \pi\right] + a \cos\left[pt + \pi\right],$$

from $t = \pi/2h$ to $t = \pi/h$. The style was removed when the maximum parabola was being drawn. If the needle had been allowed to continue tracing, its parabolic path would have gradually decreased in size until the point had reached the origin. The subsequent trace would have consisted of a series of growing parabolas drawn with the vertex in the opposite direction, the whole cycle of operations involving the drawing of the two families of oppositely-placed parabolas, each consisting of an increasing and a decreasing series.

This is illustrated in fig. 53, in which the conditions are the same except that the tracing commences with the release of the pendulums. The path of the pen is at first distorted by the elastic vibrations of the pendulum rods. The decreasing half of the first family of parabolas and the increasing half of the second family are shown on the trace, the time occupied being π/h, half the period of the complete

cycle of operations. In figs. 52 and 53, if the timing had been accurate and friction negligible, the parabolas would have been bounded by straight lines at 45 degrees to the axis of coordinates.

Still keeping the amplitudes equal and the frequencies as before, the remaining initial conditions are now changed. In fig. 54 A and C are released from their extreme outward positions by means of rods carried on the pendulums B and D. The rod on B strikes the amplitude-prop of C while a hooked rod on D releases A. A and C are released simultaneously, and in this case the style was in contact with the prepared surface from the commencement. The equations to the trace are

$$x = a \cos \left[\{2p + h\}t + \pi \right] \quad + a \cos \left[\{2p + 3h\}t + \pi \right],$$
$$y = a \cos \left[\{p + 2h\}t + 3\pi/2 \right] + a \cos \left[pt + \pi/2 \right].$$

Again neglecting frictional decrement we see that the complete trace would be bounded by the circle $x^2 + y^2 = 4a^2$. The pen was removed when $t = \pi/2h$, when the path was approximately rectilinear along the axis of y. If the trace had been continued, parabolas would have been drawn with their concavities in the opposite direction, the completed figure being symmetrical about both axes. The parabolas touch the curve

$$4 a^4 x^4 + x^2 (y^4 - 40 a^2 y^2 - 32 a^4) - 8(y^2 - 2 a^2)^3 = 0,$$

the cusps of which are on the y axis at distances $\pm a\sqrt{2}$ from the origin, the apex of the figure that we have traced coinciding with one of the two double points of the envelope. The portions of the curve between these double points constitute the effective envelope.

LIV. *The Nature of the Large Ions in the Air.* By J. A. POLLOCK, *D.Sc., Professor of Physics in the University of Sydney* [*].

IN 1905 Langevin[†] discovered that in addition to the small gas ions, with a mobility of about 1·5, there are in the air much larger ones which have a mobility of only 1/3000. Although our knowledge of the properties of these large ions is very slight, yet from the few facts which are known some deduction may be made as to the nature of the ionic structure.

The main facts are as follows:—

1. Ions with a mobility of 1/3000 under usual atmospheric conditions form a well defined class; this was Langevin's original discovery. McClelland and Kennedy * in their investigation found no evidence of any other ions. In my own measurements there is no indication of another type of ions with a mobility approximating to that of the Langevin ion, though there is a class of ions with a mobility intermediate between those of the large and small ions.

2. Langevin and Moulin † mention that the simultaneous variations in the numbers of the large and small ions in the air are opposed in direction, a fact which is also shown in the measures made on the few occasions when I have taken continuous observations of both classes of ions at Sydney. Langevin and Moulin further state that the number of the large ions is the greater the more numerous the (dust) particles in the air, and they consider the large ions as created by the attachment of small ions to these neutral particles.

From the results of C. T. R. Wilson's ‡ investigations on the formation of clouds in closed vessels, it may be inferred that these large ions do not exist in air recently freed from dust, and that they are not developed in intervals of time extending to days in dust-free air has been shown by workers in this laboratory.

3. The mobility depends on the humidity §. The first suggestion of the probability of a connexion between these ions and the moisture in the air was made by Sir Ernest Rutherford in his book on Radioactive Transformations.

These facts lead one to picture the Langevin ion as a collection of water molecules surrounding a dust particle, the whole being electrified by the attachment of a small ion. Judging from the mobility measurements, the size of the ion at constant temperature depends on the vapour-pressure. If any change of vapour-pressure occurs, the radius changes until equilibrium is again established, and there is still equilibrium when the vapour is saturated ||, for cloud condensation experiments with unfiltered air show that the ion does not grow to a visible drop until there is some slight supersaturation.

* McClelland and Kennedy, Proc. R. I. Acad. xxx. A. p. 71 (1912).
† Langevin and Moulin, *Le Radium*, iv. p. 218 (1907).
‡ C. T. R. Wilson, Phil. Trans. A. clxxxix. p. 265 (1897).
§ Pollock, Journ. and Proc. Roy. Soc. N.S. Wales. xliii. p. 198 (1909).
|| The term saturation will be used throughout to denote the condition of the vapour when in equilibrium with a plane water surface having a thickness great compared with the range of molecular force.

The large ion thus affords an interesting example of the adsorption of water vapour at a rigid surface. In connexion with such an idea it is interesting to recall a statement of Lord Rayleigh. Referring to the rise of a liquid in a capillary tube Lord Rayleigh says [*]: "Above that point (the meniscus) the walls of the tube are coated with a layer of fluid, of gradually diminishing thickness, less than the range of forces, and extending to an immense height. At every point the layer of fluid must be in equilibrium with the vapour to be found at the same level. The data scarcely exist for anything like a precise estimate of the effect to be expected, but the argument suffices to show that a solid body brought into contact with vapour at a density which may be much below the so-called point of saturation will cover itself with a layer of fluid, and that this layer may be retained in some degree even in what passes for a good vacuum. The fluid composing the layer, though denser than the surrounding atmosphere of vapour, cannot properly be described as either liquid or gaseous."

In the large ion, according to the foregoing suggestion, we have similar conditions, modified perhaps by the electrification, the equilibrium vapour-pressure depending on the thickness of the adsorbed fluid surrounding the rigid core.

To obtain some idea of the nature of the relation between mobility and vapour-pressure which is to be expected in connexion with such an ion, consider unit mass of a mixture of ions and water vapour as the working substance in a Carnot's engine. A cycle may be performed involving only reversible processes, so we have, for the mere change of state, the well known relation,

$$\left(\frac{d\phi}{dp}\right)_\theta = -\left(\frac{dv}{d\theta}\right)_p,$$

where $\phi =$ the entropy,
$p =$ the vapour-pressure,
$\theta =$ the absolute temperature,
$v =$ the volume of the working substance.

Let σ and $\sigma' =$ the density of water vapour at the saturated pressure P, and at the pressure p, respectively.

ρ, ρ' and $\lambda, \lambda' =$ the densities and latent heats of vaporization of water, and of the adsorbed fluid, respectively.

[*] Rayleigh, Phil. Mag. xxxiii. p. 220 (1892); Scientific Papers, iii. p. 523.

The relation may be written

$$\frac{\lambda'}{\theta}\left(\frac{dm}{dp}\right)_\theta = -\left(\frac{1}{\sigma'} - \frac{1}{\rho'}\right)\left(\frac{dm}{d\theta}\right)_p,$$

where m refers to the mass of the vapour.

Changing the variable this becomes

$$\frac{\lambda'}{\theta} = \left(\frac{1}{\sigma'} - \frac{1}{\rho'}\right)\left(\frac{dp}{d\theta}\right)_m . \quad \cdots \quad \cdots \quad (1)$$

If we now make the assumption that the density of the adsorbed fluid is considerable compared with that of the surrounding vapour, so that $1/\rho'$ may be neglected in comparison with $1/\sigma'$, then taking $p = \sigma'\mathrm{R}\theta$, the equation becomes

$$\frac{\lambda'}{\theta} = \mathrm{R}\theta\frac{1}{p}\left(\frac{dp}{d\theta}\right)_m .$$

For water, making a similar assumption that $1/\rho$ may be neglected in comparison with $1/\sigma$, we have

$$\frac{\lambda}{\theta} = \mathrm{R}\theta\frac{1}{\mathrm{P}}\frac{d\mathrm{P}}{d\theta} ,$$

so

$$\frac{\lambda'}{\lambda} = \frac{\frac{1}{p}\left(\frac{dp}{d\theta}\right)_m}{\frac{1}{\mathrm{P}}\left(\frac{d\mathrm{P}}{d\theta}\right)} .$$

Putting $\lambda'/\lambda = 1/n$ we may write

$$\frac{1}{p}\frac{dp}{d\theta} = \frac{1}{n\mathrm{P}}\frac{d\mathrm{P}}{d\theta} .$$

If at two temperatures, θ_1 and θ_2, corresponding values are p_1 and P_1, p_2 and P_2, then integrating we have

$$\left(\frac{p_2}{p_1}\right)_m = \sqrt[n]{\frac{\mathrm{P}_2}{\mathrm{P}_1}}.$$

That is, the mass of adsorbed fluid, and consequently the mobility, will be the same at a temperature θ_2 as at a temperature θ_1 if the new vapour-pressure is

$$p_2 = p_1\sqrt[n]{\frac{\mathrm{P}_2}{\mathrm{P}_1}}.$$

This equation, according to the assumptions which have been made, is the formula for reducing the observed mobilities to a common temperature, and thus affords a basis for a discussion of the observations.

Table I.* contains the observed values of the reciprocals of the mobilities, reduced to standard atmospheric pressure, together with the temperature and vapour-pressure at the time the observations were made.

TABLE I.

$1/u$.	t. Cent.	P_t. mm.	p_t. mm.	p_{20}. mm.
		Grouped results.		
1253	18·3	15·62	0·60	0·67
1802	18·8	16·12	5·45	5·87
3077	16·3	13·77	11·81	14·90
3155	23·2	21·11	18·86	15·51
3226	15·9	13·42	12·41	16·05
		Single observations.		
2310	15·3	12·95	6·60	8·85
2570	20·9	18·04	10·64	10·24
2640	20·1	17·22	11·02	11·11
2725	23·5	20·94	14·24	11·80

Values of the reciprocals of the mobilities of the large ions reduced to standard atmospheric pressure, and the temperature and water-vapour pressure at the time the observations were made, together with the vapour pressure reduced to 20° C.

The single observations are those depending on one day's measures only, natural air being used. For these determinations the humidity was calculated from the wet and dry bulb readings; whereas in the case of the grouped measures where the moisture in the air was artificially controlled, the humidity was found by absorbing the water vapour and weighing. The estimations of the humidity by the wet and dry bulb readings now appear to be low, though from a comparison of the two methods of determining the humidity, made at an early stage of the investigation, no constant difference was apparent.

When the humidity changes, the ions do not at once reach a stage of equilibrium with the new vapour-pressure conditions, and in the determinations, when a change of humidity occurred, 13 minutes were allowed to elapse before the measurements for mobility were made. In reviewing the observations, I think it is possible that this interval may not have been long enough in the case represented by the first

* For details see Journ. and Proc. Roy. Soc. N. S. Wales, xliii. pp. 61 and 198 (1909). A single observation, given in one of the tables previously published, has been omitted, as on looking up the original records the result is found to be unreliable.

entry in the table, so the estimated value, 1253, of the reciprocal of the mobility for a humidity of 4 per cent. may be too large.

As a determination of mobility requires the measurement of a series of ionization currents, the investigation is a tedious one in the case of the natural large ions where the ionization is not under control and is subject to considerable variations. The values given in Table I. represent the results of observations on the few occasions, during two and a half years or more, when the ionization was sufficiently constant in this laboratory for the purpose of the calculation.   Under the conditions a very exact comparison of the theoretical deduction with observation is not possible.

It can be said at once, however, that the observations show that λ/λ', or n in the reduction formula, must be very nearly equal to unity, and on the assumption that it is so, the pressures corresponding to the mobilities in Table I. have been reduced to a common temperature of 20° C., and are entered in the table.

Fig. 1.
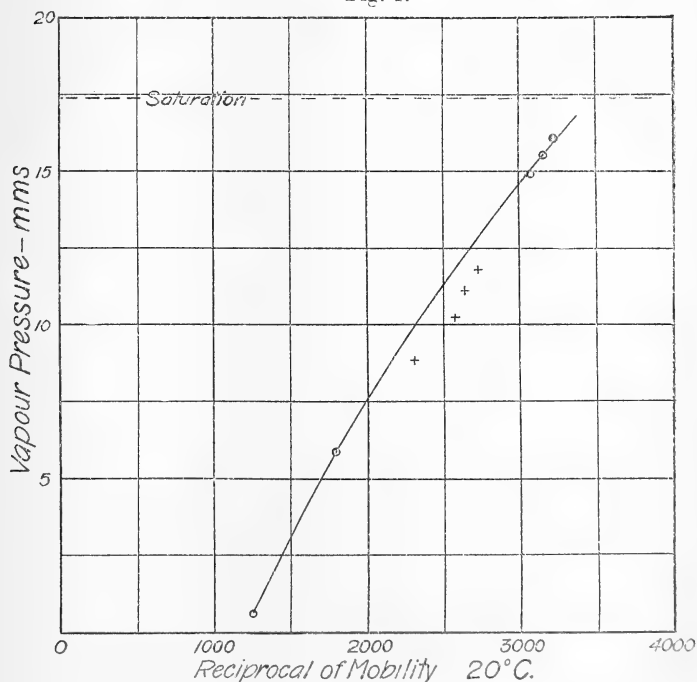
From these reduced observations fig. 1 has been drawn; the curve therefore shows the relation between the reciprocal

of the mobility, reduced to standard atmospheric pressure, and the water-vapour pressure for a temperature of 20° C. The single observations have been included, but they are not to be considered as of equal weight with the grouped measures.

A second approximation to the value of n is now possible for the part of the curve in fig. 1 corresponding to a pressure of about 15 millimetres. It appears here that the fit of the points to the line is perceptibly better when n is taken as 1 than when it is taken as $1 + \cdot 01$, and noticeably better than when it is put equal to $1 + \cdot 0\overline{3}$.

For the large ions, then, to a considerable degree of accuracy the mobility remains the same as the temperature varies, if the equilibrium vapour-pressure is a constant fraction of the saturated vapour-pressure for a plane surface; or, in other words, the mobility at standard atmospheric pressure is a function of the relative humidity only.

This relation may be written

$$\frac{1}{p}\left(\frac{dp}{d\theta}\right)_m = \frac{1}{\mathrm{P}}\frac{d\mathrm{P}}{d\theta},$$

and in this form is similar to the relation found by Trouton[*] between the equilibrium vapour-pressure and the mass of contained moisture in the case of flannel and cotton-wool, and independently discovered by Masson and Richards[†] during a very accurate investigation with this latter material.

The determination that the ratio of λ to λ' is approximately unity in the case of the large ions enables a deduction to be made as to the condition of the adsorbed moisture, for with its latent heat nearly equal to that of ordinary water it seems impossible to consider the adsorbed fluid other than in the liquid state.

Trouton[‡] has shown that there are two possible modes of condensation of water vapour on rigid surfaces. If special precautions are taken in drying the surfaces, on exposure to water vapour, a gaseous form of condensation occurs, which changes somewhat abruptly to the liquid form at a vapour-pressure depending on the nature of the surface. In the case of the gaseous form of condensation, one would imagine that the ratio of the latent heat of water to the latent heat of vaporization of the dense vapour, or n in the formula of reduction, would be much greater than unity. Insofar as

* Trouton, Proc. Roy. Soc. A. lxxvii. p. 292 (1906).
† Masson and Richards, Proc. Roy. Soc. A. lxxvii. p. 412 (1907).
‡ Trouton, Proc. Roy. Soc. A. lxxix. p. 383 (1907); Chem. News, 96. p. 92 (1907).

the density of the vapour is small in comparison with the density of the adsorbed moisture, the value of n found necessary for the reduction of adsorption observations to a common temperature might, therefore, possibly form a criterion in determining the condition of the absorbed fluid.

This question of the condition of the adsorbed moisture is even capable of somewhat more precise consideration, for in the case of the large ions, and of uncharged drops of a similar nature, which as shown by cloud condensation experiments do not become unstable until the vapour becomes, at least, slightly supersaturated, equation (1) becomes

$$\frac{\lambda'}{\theta} = \left(\frac{1}{\sigma} - \frac{1}{\rho'}\right)\frac{dP}{d\theta},$$

and no doubt the equation also holds for fluid adsorbed at a plane surface.

Putting $\rho' = \rho + \delta\rho$ with the sign of $\delta\rho$ undetermined, the expression may be written

$$\frac{\lambda'}{\theta}\left(1 + \frac{\delta\rho}{\rho}\right) = \frac{\rho - \sigma}{\rho\sigma}\frac{dP}{d\theta}\left(1 + \frac{\delta\rho}{\rho - \sigma}\right),$$

or

$$\frac{\lambda'}{\lambda} = \frac{1 + \dfrac{\delta\rho}{\rho - \sigma}}{1 + \dfrac{\delta\rho}{\rho}}.$$

At atmospheric temperatures, as σ is small compared with ρ, we see, without requiring a knowledge of the density, that when the vapour-pressure is that of saturation the adsorbed fluid has a latent heat differing very little from that of water. From the point of view of Laplace's theory it is difficult to see how this conclusion could fail to carry with it the inference that the difference in density is also small.

If it is experimentally found that $(1/p)(dp/d\theta)_m$ is equal to $(1/P)(dP/d\theta)$ for all values of p, then

$$\frac{\lambda'}{\lambda} = \frac{1 - \dfrac{\sigma'}{\rho'}}{1 - \dfrac{\sigma}{\rho}}$$

for all values of the vapour-pressure.

If the adsorbed fluid is in the liquid state, little change, I believe, occurs in its density as the vapour-pressure alters.

so for low pressures σ'/ρ' may be neglected in comparison with σ/ρ, and as a first approximation we have here

$$\chi' = \lambda \left(1 + \frac{\sigma}{\rho} \right).$$

At all pressures it would appear, then, that if the adsorbed fluid is in the liquid state, it has a latent heat and a density very little different from those of water.

It must be mentioned that the preceding thermodynamic argument was first applied in this connexion by Trouton in the earlier of his papers quoted ; I use it here, however, in the converse form to that in which it was employed by him.

The large ion, then, may be considered as a rigid core surrounded by a film of water rather than by a dense atmosphere of water molecules, though of course the transition layer from water to vapour must be an important feature.

An estimate of the diameter of the ion may be made, in the light of a knowledge of the mobility, by considering the resistance which the molecules of the surrounding gas offer to the motion of the ion in an electric field; but, on account of the assumptions which are involved in any such application of the principles of the kinetic theory as outlined below, the result of the calculation must be taken as giving merely the order of magnitude.

According to the work of Langevin[*] in this connexion, amended by H. A. Wilson[†], the velocity of an ion in a field of unit intensity is given by the expression

$$u = 1 \cdot 4\, e l_1 / m_1 v_1,$$

where e is the ionic charge, l_1 the mean free path of the ion, m_1 its mass, and v_1 its mean velocity of thermal agitation. The size of an ion, however, cannot be calculated merely from a knowledge of the mobility, and we are forced to follow the converse method of assuming size and mass and calculating mobility. To obtain a suitable expression for this purpose, let s_1 be the diameter of the ion, s_2 that of the air molecule, and in general let the subscripts 1 and 2 refer to ionic and molecular quantities respectively.

From the kinetic theory we have [‡]

$$l_1^{-1} = \pi n_2 \left(\frac{s_1 + s_2}{2} \right)^2 \sqrt{1 + \frac{m_1}{m_2} \left(1 + \frac{2\mathrm{M}}{m_2 v_2} \right)},$$

* Langevin, *Ann. de Chim. et de Phys.* vii. p. 335 (1903).
† H. A. Wilson, Phil. Mag. xx. p. 385 (1910).
‡ See Wellisch, Phil. Trans. A. ccix. p. 272 (1009) ; also Lusby, Phil. Mag. xxii. p. 784 (1911).

where n_2 is the number of air molecules per cubic centimetre, and M the mutual potential energy at collision of ion and molecule due to the ionic charge. In the case of the large ion, on account of its size, M will no doubt be very small compared with $m_2 v_2$, and the last factor in the above expression will be neglected in this discussion as probably differing little from unity.

Let
$$x = \frac{s_1}{s_2}, \quad y = \frac{m_1}{m_2},$$

then with well known substitutions the expression for the reciprocal of the mobility may be written

$$\frac{1}{u_t} = \frac{\rho_0 p}{8 N_0 e \eta} (1+x)^2 \sqrt{y(1+y)},$$

where N_0 is the number of air molecules per cubic centimetre and ρ_0 the density of air under standard conditions, η the viscosity at the temperature t° C., and p the air pressure. The modification of this formula so that it may include the effect of the persistence of velocities after collision is doubtless a small one, and may be neglected for the present purpose.

The diameter of the ion as calculated by the preceding expression does not vary greatly for moderate changes in the density, so, in view of the lack of any knowledge of the core, limits to the diameter of the ion according to this method of estimation are set out in Table II. for various values of the mobility, by assuming firstly that the ion is all water, and secondly that the density of the whole is 2·5, this figure being considered as possibly the value of the density of the core.

If the resistance to the motion of the transition layer is not negligible compared with that offered to the motion of the ion as a whole, then the diameter of the liquid part of the drop corresponding to any mobility will be less than that given in the table, and the mass greater than that indicated by the diameter.

The calculation has been made from the following data :—

$N_0 e = 1\cdot 29 \times 10^{10}$ E.S.U., $s_2 = 2\cdot 9 \times 10^{-8}$ (diam. of air molecule),

$\eta_{20} = 1\cdot 80 \times 10^{-4}, \qquad m_2 = 4\cdot 7 \times 10^{-23}$ (mass ,,   ,,   ),

$\rho_0 = 0\cdot 001293, \qquad\qquad$ volume of ion $= \frac{4}{3} \pi \left(\frac{s_1}{2}\right)^3,$

$p = 1\cdot 0132 \times 10^6.$

TABLE II.

p/P per cent.	$1/u$.		$\rho'=1$.		$\rho'=2.5$.	
		s_1/s_2.	s_1.	s_1/s_2.	s_1.
4·0	1250	11·4	$3·3\times10^{-7}$	9·4	$2·7\times10^{-7}$
43 2	2000	12·5	3·6 ,,	10·4	3·0 ,,
83·5	3000	13·6	3·9 ,,	11·3	3·3 ,,
100·0	3440	14·0	4·1 ,,	11·6	3·4 ,,

Diameters of the large ion for various values of the mobility.

For equilibrium, under usual atmospheric conditions, the value of the free surface energy must be influenced by the attraction of the core, so the thickness of the surrounding film of water cannot, from this point of view, be great compared with the range of molecular force. The preceding calculation makes the diameter of the whole ion about a tenth of the value, 5×10^{-6} centimetre, usually accepted for this range. The nuclei of these large ions may, then, be very minute, and although their actual size is unknown it is possible that they may be fairly uniform in diameter, as there is evidence that the mobilities of the fully developed ions under given atmospheric conditions lie within somewhat narrow limits.

It is not quite clear how the electrical energy of the ions is related to their diameter. The charge is, however, not necessary for equilibrium, and it is not unlikely that the conclusions as to the nature of the ions, only rendered possible by the happy chance of their electrification, may apply with perhaps little modification to many of the far more numerous class of unelectrified nuclei which exist in ordinary air.

A detailed discussion of the large ion was published by Sutherland in the Philosophical Magazine for September 1909. In his own words his view is as follows * :—"To account for the very small mobility of the large ion of Langevin I have imagined the structure already described, namely, a nucleus of $(H_2O)_2$ or $(H_2O)_3$ or both in a state very similar to that of a liquid surrounded by an envelope of H_2O vapour which is kept highly concentrated close to the nucleus. This envelope is similar to the surface film of vapour of H_2O deposited on the grains of fine powders. The number of H_2O molecules per cm.³ close to the nucleus

* Sutherland, Phil. Mag. xviii. p. 366 (1909).

will have a value N_{2s} like a saturation value, and the number will diminish with increasing distance from the nucleus till it becomes N_2 where its influence has ceased."

For the velocity u of the ion in an electric field he gives the expression

$$e\frac{d\mathrm{E}}{dx} = r^2 q^{2/3}\mathrm{N}_3\mathrm{T}^{1/2}(\mathrm{EN}_2 + \mathrm{G} + \mathrm{HN}_2)u,$$

where r is the distance between the centres of a molecule of H_2O and one of air when in collision, q the number of ions, and N_3 the number of air molecules, per cubic centimetre, T the absolute temperature, and E, G, and H, on the right-hand side of the equation, constants.

The form of the expression within the brackets was suggested by a preliminary result of my own measurements that

$$1/u = 1200 + 107\cdot5\,h,$$

where h is the humidity in grammes per cubic metre. Such a form of relation only holds approximately as may be seen from an inspection of fig. 1, and the numerical values in the equation need modifying in the light of the later measures, and may require considerable alteration if it turns out that the observations at low humidities require correction.

Stress is laid by Sutherland on the point that according to his view of the movement of gaseous ions the mobility should depend on the density of ionization. In my observations the number of ions per cubic centimetre varied from 650 to 32900, but no dependence of mobility on this factor is apparent.

Sutherland's discussion has the great merit that it involves no unreasonable assumptions. It was developed, however, before the evidence in favour of a rigid core in connexion with the large ions was fully appreciated, and from what I have said in this paper I believe his investigation requires modification.

A correspondence with this gifted author during the progress of the experimental work was a source of great encouragement in a most tedious investigation.

Summary.

1. The large ions in the air, which were discovered by Langevin in 1905, have a mobility which at constant atmospheric pressure is a function of the relative humidity only. At standard pressure the mobility varies from $1/1250$ when the humidity is 4 per cent., to $1/3440$ when the pressure is that of saturation.

2. The ions do not exist in dust-free air, so the picture most readily formed is that of a collection of water molecules surrounding a dust particle, the whole being electrified by the attachment of a small ion. The ion thus affords an interesting example of the adsorption of water vapour at a rigid surface.

3. A thermodynamic argument, based on the relation between mobility and relative humidity, leads to the conclusion that the adsorbed moisture is in the liquid state with a latent heat and density little different from those of water.

4. The order of magnitude of the diameter of the ion, as calculated on usual kinetic theory lines, varies from 3 to 4×10^{-7} centimetre according to the atmospheric conditions.

The Physical Laboratory,
 The University of Sydney,
 November 25, 1914.

LV. *On the Motion of a Sphere in a Viscous Fluid.* By W. ELLIS WILLIAMS, *B.Sc., A.F.Aë.S., University College, Bangor* *.

[Plate IX.]

NOTATION :—

μ ...... coefficient of viscosity.

$\nu = \mu/\rho$ .. kinematic coefficient of viscosity.

V ..... velocity of sphere.

a ..... radius of sphere.

R, Θ .... velocities along the polar coordinates r, θ.

u, w .... velocities along the cylindrical coordinates ϖ, z.

ψ ...... Stokes's current function.

p ..... pressure at a point in the fluid.

THE mathematical solution of the problem presented by the motion of a solid body moving with finite velocity through a viscous fluid has hitherto presented insuperable difficulties, and no solution has been obtained even for the apparently simple cases of a sphere or cylinder moving with uniform velocity along a straight line. The complicated nature of the equations of motion together with the difficulties presented by the boundary conditions, which require that both the normal and tangential velocities should have specified values at the surface of the moving body, seem to place the direct solution of the problem far above the reach of any known method. The actual solutions of the problem which are given in the current text-books of hydrodynamics are

* Communicated by Prof. E. Taylor Jones, D.Sc.

obtained by ignoring some of the terms in the general equations of motion, and thus simplifying them to such an extent that a direct mathematical solution is possible.

These solutions may be divided into two classes, which may be looked upon as limiting cases of very high and very low velocities respectively. The equations of motion of an incompressible fluid as obtained by Navier and Poisson may be written :—

$$\frac{\partial u}{\partial t} = X - \frac{1}{\rho}\frac{\partial p}{\partial x} - u\frac{\partial u}{\partial x} - v\frac{\partial u}{\partial y} - w\frac{\partial u}{\partial z} + \nu\nabla^2 u, \quad . \quad . \quad (1)$$

with similar equations for the other coordinates (X, Y, Z are the components of the impressed forces).

The right-hand sides of these equations contain terms such as $u\frac{\partial u}{\partial x}$, which are of the second power in the velocity, and also terms such as $\nu\nabla^2 u$, which are of the first power ; if, therefore, in any case the velocity is large and the coefficient of viscosity ν is small, the terms $\nu\nabla^2 u$ &c. may be neglected, and we thus arrive at the so-called "perfect fluid" or irrotational equations. These equations can be solved for a large variety of boundary conditions, and it is these solutions which take up the greater part of the current text-books of hydrodynamics. It is found, however, that the actual motion observed is, in general, very different from that given by the solutions thus obtained, a difference which is perhaps most glaringly shown by the fact that, according to the perfect fluid theory, a body moving with uniform velocity experiences no resistance to its motion.

This discrepancy is usually ascribed to the occurrence of "cavitation." At sharp corners and edges the theory makes the velocity of the fluid infinite, the pressure in the fluid has consequently a large negative value, a cavity is formed around the edge, and the instability of the motion around this cavity is supposed to cause a general breakdown of the motion. Without denying the fact that cavitation may occasionally occur, and that its occurrence may alter the whole motion, a careful survey of the experimental facts available will show that the above explanation is totally inadequate. In the first place, the motion of the fluid surrounding a moving body is (at ordinary velocities) the same for air and for water, due regard being paid to the different densities and viscosities, and the irrotational solutions are no more applicable to air than to water. It is difficult, however, to imagine anything resembling cavitation taking place

in air, and, in fact, the lowest pressures experimentally observed on aeroplane wings and similar bodies are never more than a few cms. of water below atmospheric pressure. In the second place, the difference is by no means confined to cases in which sharp edges are present, but is quite as great when the moving bodies are spherical or cylindrical so that cavitation cannot take place even in heavy liquids, and, in fact, the difference may be shown to exist in cases where the absence of cavitation may be experimentally demonstrated.

The reason for the discrepancy appears to lie rather in the nature of the boundary conditions and the impossibility of satisfying them in the irrotational solutions. All the experimental evidence available goes to show that for fluids such as water and air the particles of fluid in the immediate neighbourhood of a solid boundary have no motion relative to that boundary, while the irrotational solutions cannot be made to satisfy this condition owing to the fact that, viscosity being neglected, tangential motion gives rise to no stress, so that in general the solutions indicate a large amount of slipping at the boundary.

In the case of solids of "stream-line" or fish-like shape the motion appears to be similar to that given by the irrotational solution except in a layer of fluid in the neighbourhood of the surface of the moving body [*]. In this layer, which is relatively thin, the velocity changes rapidly from the value given by the boundary condition to that given by the irrotational solution. Within this layer the value of $\dfrac{\partial^2 u}{\partial x^2}$ is therefore large compared with u and the term containing the viscosity is no longer negligible. The high value of the space differential of the velocity gives rise to a considerable tangential force on the surface of the body, which is generally known as "skin friction."

In most cases, however, the transition layer is not confined to the surface of the moving body, but departs from it near midsection and gives rise to a "wake" of eddying motion, which persists in the fluid for a considerable distance behind the moving body, completely altering the character of the motion.

In certain cases the motion may be approximately represented by the assumption of surfaces of discontinuity in the fluid, and the solutions obtained in this way by Kirchhoff and Rayleigh, though far from giving an exact representation of the observed motion, are yet a great advance on the older theory. The methods developed do not, however, throw any

[*] *Vide* Prandtl, *Handbuch d. Naturwiss.* iv.

light on the way in which these surfaces arise or enable us to decide in what cases they will occur.

If, instead of neglecting the terms of the form $\nu\nabla^2 u$ in the equations of motion, we retain these and neglect those of the type $u\dfrac{\partial u}{\partial x}$, the equations reduce to a form which can be solved for certain cases, and give solutions which are applicable when the velocities are small and the viscosity high.

The most important of these solutions is that for a sphere moving in a straight line, obtained by Stokes in his memoir on the motion of pendulums. It was shown by Rayleigh that this solution may be expected to hold so long as $\mathrm{V}a/\nu$ is small compared with unity, and experiments by Ladenburg[*] and others show that when due account is taken of the boundary conditions the resistance formulæ derived from the solution agree with the experimental results to a very high degree of accuracy. The limiting velocity thus defined is, however, very low, and the practical applications of the solutions are confined to motion in very viscous fluids.

An attempt has been made by Whitehead[†] to obtain a second approximation to Stokes's solution by expanding the neglected terms in powers of the velocity, and taking account of second powers only. The method, however, does not lead to any definite results, as the vorticity becomes infinite in certain parts of the field. This is taken by him to indicate that the motion becomes unstable and breaks down suddenly in the neighbourhood of the critical velocity, and that eddying motion involving high values of vorticity is set up. It will be seen later that this explanation cannot be reconciled with experimental results.

It will be gathered from the above that nothing is really known as to the nature of the motion for values of the velocity which are neither very high nor very low, and the investigations described below were undertaken with the object of throwing some light on this problem, and in particular to determine the way in which the motion changes as the velocity is increased beyond the critical value.

The problem has been approached both from the experimental and theoretical sides, and in order to simplify matters as far as possible the investigations have been confined to the case of a sphere moving with uniform velocity along a straight line. The actual motion of the fluid surrounding

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[*] Ladenburg, Diss. Munich, 1906.
[†] Whitehead, Quart. Journ. Maths. 1889, p. 143.

the moving sphere has been observed, and it has been found possible to photograph the motion and to map out the stream-lines for velocities up to 720 times the critical value. At the same time certain mathematical solutions have been obtained which serve to throw some light on the changes which take place in the form of the motion as the velocity increases beyond the critical value. We shall first describe the methods by which the stream-lines were experimentally observed and measured, and then proceed to describe the results and to compare them with the solutions obtained. The greater part of the experiments was carried out with a sphere moving in water, but in order to obtain measurements over as wide a range as possible it was found desirable to use liquids of different viscosities. The advantage of doing this lies in the fact that irregular currents are set up in the liquid by the inevitable slight differences of temperature of different parts of the trough, and accurate measurements are impossible if these currents have a velocity which is an appreciable fraction of the velocity of the sphere. It was found that the lowest practicable velocity in water was about 1 cm. per sec., which gave $Va/\nu = 23$, and it was thus impossible to work in the immediate neighbourhood of the critical velocity. After trying a number of different liquids, it was found that good results could be obtained by using mixtures of glycerine and water in different proportions according to the viscosity desired. For pure glycerine the value of ν is about 15 and all values between this and ·013, the value for water, may be obtained by suitably adjusting the proportions of water and glycerine in the mixture. The viscosity of the mixture was determined in each case by means of an Ostwald viscosimeter.

The experiments were carried out with two rectangular troughs of similar shapes but of different dimensions. The smaller trough was of glass and measured $19 \times 10 \times 9$ cm., and was used for the glycerine experiments, while the larger trough was of wood with glass face and ends and measured $46 \times 18 \times 17$ cm. The radii of the spheres used were 1·25, ·88, and ·40 cm. respectively. The experimental results obtained with different spheres and liquids can be correlated by means of the dimensional theorem :—The motion in any two liquids with geometrically similar boundaries is similar when the quantity Va/ν is the same in the two cases. In what follows, therefore, the value of this quantity is given for each result. In the experiments Va/ν varied from ·01 to 720.

The general arrangement of the apparatus is shown in fig. 1. The trough T was placed on a table fixed to the wall of the room. Above it was a long frame AB resting on the rollers RR, and the sphere S was attached to a piece

Fig. 1.
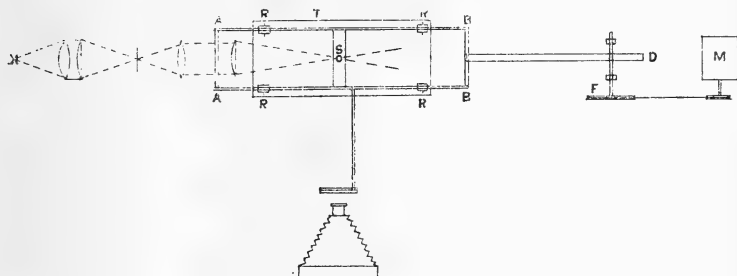
Arrangement of apparatus.

of steel wire fixed to the middle of the frame, so that the latter in moving along on the rollers carried the sphere from one end of the trough to the other. The position of the sphere was adjusted so that its centre moved along the centre line of the trough. Motion is given to the frame by means of a heavy bar, BD, hinged to it and resting on the axle of the pulley F, which is connected by a set of reduction-pulleys to the axle of a small electric motor, M. The velocity of the frame can be varied by varying the resistance in the armature circuit of the motor and also, if necessary, by varying the reduction ratio of the connecting pulleys. The motor was kept continually running and the frame started by dropping the bar on the axle. The frame being very light it immediately took up the velocity of the axle, and thus the sphere moved along the trough with a uniform velocity.

The motion of the liquid is rendered visible by mixing up a little aluminium powder with a drop of glycerine and stirring it into the liquid in the trough. The little aluminium flakes remain suspended in the water for several hours, and when illuminated by a beam of light from an arc lamp show clearly the motion of the liquid surrounding the moving sphere.

A camera was arranged in front of the trough, and when the motion is photographed the aluminium particles trace out curves on the plates which serve to measure the velocity of the fluid and enable the stream-lines to be plotted out.

The arrangement of the illumination and exposure was somewhat different for the two troughs. The small trough being used chiefly for low velocities, the exposures required were long enough to be made by hand, and the beam of light was strong enough to illuminate the whole field of motion. Considerations of symmetry show that the motion must be the same in any plane passing through the axis defined by the path of the centre of the sphere, and hence it is sufficient to investigate the motion in one such plane. A beam of light from the condenser placed in front of the arc-lamp E is focussed on a slit G and then rendered approximately parallel by passing through a cylindrical lens formed by a tall narrow beaker full of water; it is then narrowed down by a vertical slit placed on the end of the trough, and passes through the trough as a thin vertical sheet of light illuminating the central plane of the liquid in the trough. The camera is placed directly in front of the trough and is focussed on the sphere and the illuminated plane. If a plate is exposed for a short time while the sphere is in motion, each little aluminium particle will trace out a curve on the plate. This curve will be practically a short straight line, and the ratio of its length to that of the trace of the sphere itself will give the velocity of the particle, which, owing to the lightness of the particle, is also that of the surrounding fluid. The photographs A–C reproduced in Plate IX. give an idea of the results obtained by this method.

The larger trough was used for the higher velocities, and the above method could not be adopted with it as the beam of light had to be made much more intense to get good photographs, and hence only a small portion of the field could be illuminated, and it was necessary to take several photographs of different parts of the field and then combine them together to give a stream-line diagram. The beam of light in this case passes through both a cylindrical and a convex lens and enters the trough as a convergent beam with a vertical-line focus near the centre of the trough. In the neighbourhood of this focus the beam gives a very strong illumination over a field about 2 cm. each way, the average thickness of the illuminated plane being about 2 mm. By suitably inclining the beam and altering its focus by moving the lenses, the illuminated portion could be brought to any desired part of the trough, and thus, by taking a number of photographs, the whole of the central plane can be covered. The camera is placed in front of the trough as before, but the exposure is made by a shutter attached to the lens which is automatically released

. by the motion of the frame when the sphere has reached the centre of the trough. The duration of the exposure can be varied to suit the velocity of the sphere, and the length of the trace gives the velocity as before. About half a dozen photographs were required to cover the whole field, and these were combined and measured by the following method. A circle of 2·5 cm. radius was drawn in the middle of a sheet of squared paper, which was then set up on a drawing-board in front of a projecting lantern. One of the plates was placed in the lantern and a magnified image of the plate thrown on the paper, this was then adjusted so that the mean position of the ball during the exposure coincided with the circle drawn on the paper, the magnification being adjusted so that the diameter of the image was exactly 5 cm. The length of each trace was then measured with a pair of dividers and its direction marked on the paper. Each plate of a series was put into the lantern in turn, and thus the whole field of motion was mapped out.

The motion is best represented by means of Stokes's current function ψ. If the motion be referred to cylindrical coordinates z, ϖ, the line traced out by the centre of the sphere being taken as axis of z and the corresponding velocities being denoted by u, w, then ψ is defined by

$$w = \frac{1}{\varpi}\frac{\partial \psi}{\partial \varpi}, \quad u = -\frac{1}{\varpi}\frac{\partial \psi}{\partial z},$$

and hence the curves $\psi = $ const. give the direction, and their distances apart divided by ϖ give the magnitude of the velocity at any point. The values of ψ for the median line $z = 0$ and for the surface of the sphere were first calculated from the measurements of velocity, and starting from points giving $\psi = ·2, ·4$, &c., the curves were drawn in the direction of the velocity as marked on the paper, and thus the stream-line diagrams of figs. 2–8 were obtained. In each diagram the straight line at the bottom is for $\psi = 0$ and each succeeding curve is for values of ψ increasing by an interval of ·2, the velocity of the sphere being always taken as unity.

The results obtained are shown in the accompanying diagrams and photographs which we may now proceed to describe in detail.

The first two diagrams figs. 2 and 3 and the corresponding photograph A (Pl. IX.) refer to a sphere moving with a

velocity of ·13 cm. per sec. in glycerine. Fig. 2 is for
a sphere of ·8 cm. radius moving in the smaller glass trough,

Fig. 2.
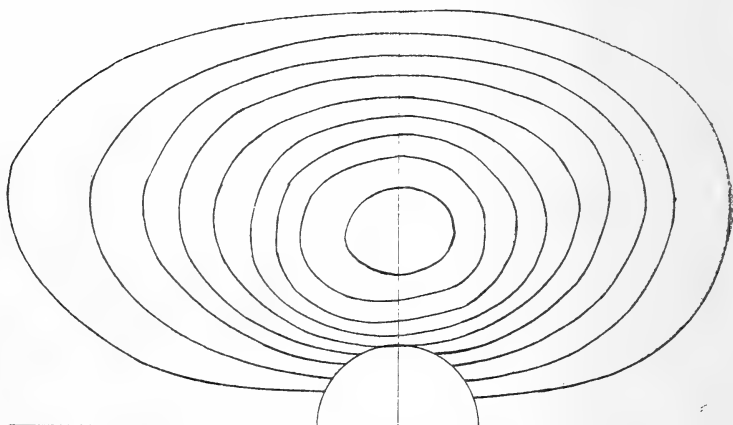
Sphere in glycerine, $Va/\nu = ·0116$ (Experimental).

while fig. 3 is for the same sphere moving in a cubical
trough measuring $10 \times 10 \times 10$ cm., this latter being taken
for comparison with a theoretical result to be given later.

Fig. 3.
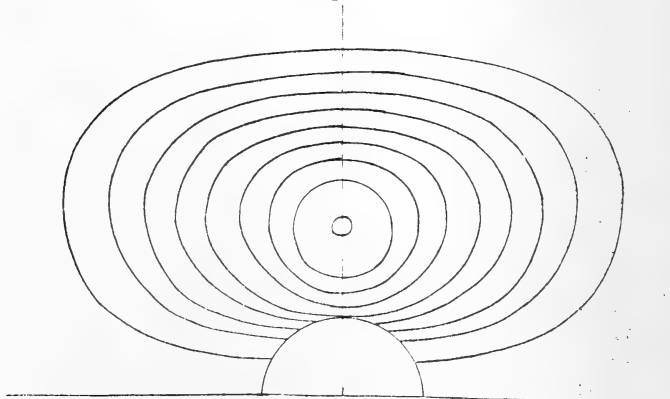
Sphere in cube, $Va/\nu = ·0116$ (Experimental).

The kinematic coefficient of viscosity was found to be 10 c.g.s.
units, and the value of Va/ν is therefore ·0116 or rather more
than 1 per cent. of the critical velocity. The motion should

thus be accurately represented by a solution obtained by neglecting the inertia terms. If, however, the lines of fig. 2 be compared with the diagram of Stokes's solution given on p. 532 of Lamb's 'Hydrodynamics' it will be seen that the observed motion differs widely from the theoretical diagram. This is obviously due to the effect of the containing vessel on the motion, Stokes's solution referring to a sphere moving in a fluid extending to infinity. It may in fact be shown that the effect of the boundary is appreciable even when the sphere is small compared with the vessel. The velocity in Stokes's solution is everywhere in the same direction as that of the sphere, while if we consider the flux across the median plane perpendicular to the motion, it is obvious that the total amount of fluid crossing the plane must be zero at every instant (the sphere itself being reckoned as though it were fluid) ; hence the forward motion of the liquid near the sphere must be compensated by a backward flow in the outer portions of the vessel. As the velocity of the fluid only diminishes with the first power of the distance, the effect is very marked even when the vessel is very large compared with the sphere. This in fact is what we see in the photograph ; in the immediate neighbourhood of the sphere the fluid moves along with it, but as we go away from the sphere we see that the velocity diminishes to zero and in the outer parts of the vessel is mainly in the opposite direction.

Fig. 4.
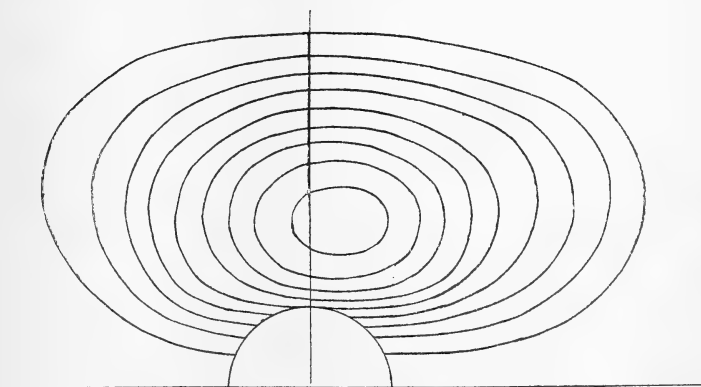
Sphere in glycerine, $Va/\nu = 2\cdot1$ (Experimental).

Passing on to the diagram of fig. 4 and the corresponding photograph B, Pl. IX., these refer to a velocity of ·217 cm. per sec. in a mixture of glycerine and water of viscosity $\nu = \cdot09$. The value of Va/ν is therefore $2\cdot1$ and the critical

value has therefore been passed.   It will be noticed that the
form of the stream-lines has changed slightly.   The diagram
is no longer symmetrical about the median plane, but the
point of zero velocity and the stream-lines which centre on it
have moved so as to be behind the centre of the sphere.
The velocity in front of the sphere is accordingly diminished
and that behind it increased.   The change is much more
marked in fig. 5, Photo C (Pl. IX.), which corresponds to a
velocity of ·38 cm. per sec. in the same mixture.

Fig. 5.
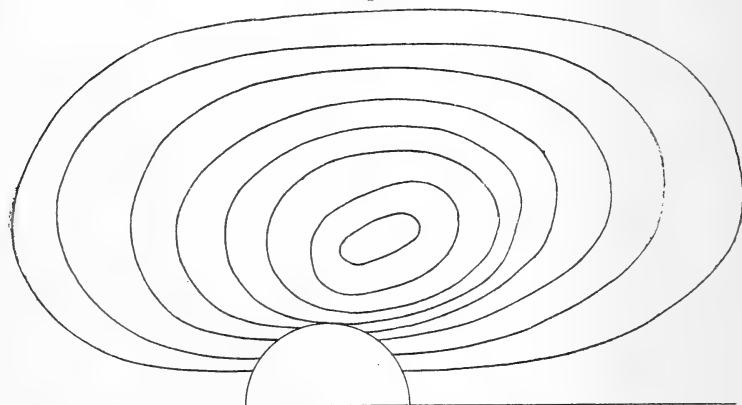
Sphere in glycerine, $Va/\nu = 3.7$ (Experimental).

Va/ν is now 3·7, and it will be seen that the point of zero
velocity has moved still further back and that the stream-lines
around it are somewhat elongated instead of being approxi-
mately circular as in the previous diagrams.

Fig. 6.
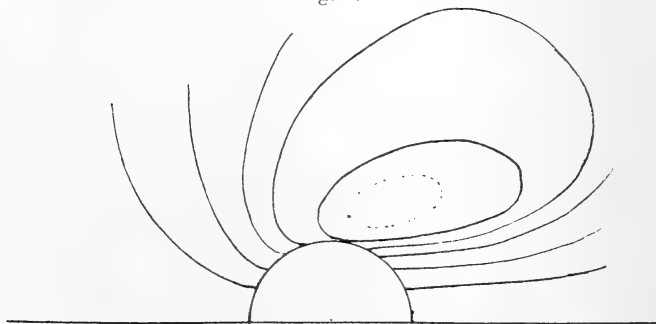
Sphere in water, $Va/\nu = 23$ (Experimental).

In fig. 6, Photo D (Pl. IX.) we get the first of the results
for water.   The velocity is ·24 cm. per sec., and the value

of Va/ν is 23. In this figure it will be seen that point of zero velocity has approached nearer to the sphere and also moved still further back, the stream-lines around it being nearly elliptical; the increase of velocity behind the sphere is very marked, the velocity of the fluid being nearly the same as that of the sphere for a considerable distance behind it.

In the case shown in fig. 7 the velocity has been increased to 1·3 cm. per sec., the corresponding value of Va/ν being 125. The point of zero velocity has come almost into line

Fig. 7.
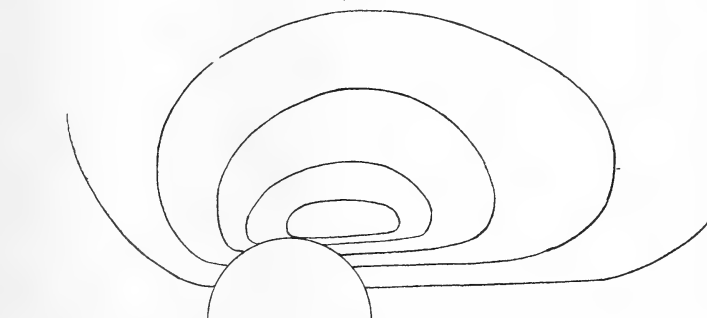
Sphere in water, $Va/\nu = 125$ (Experimental).

with the top of the sphere. The velocity in front of the sphere is very similar to that in the irrotational solution (see Lamb, p. 137), and behind the sphere is seen a " wake " of nearly constant velocity as shown by the parallel stream-lines.

Fig. 8.
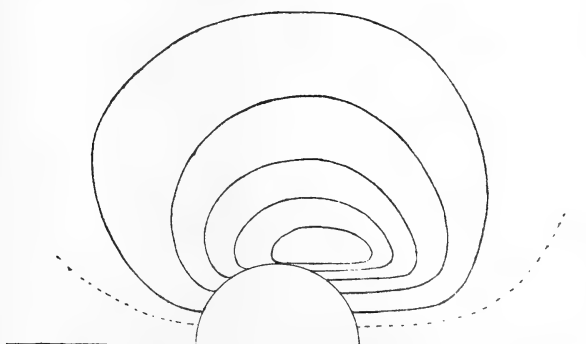
Sphere in water, $Va/\nu = 720$ (Experimental).

Fig. 8, Photo E (Pl. IX.), represents a velocity of 7·5 cm. per sec., the corresponding value of Va/ν being 720. In this case the wake is considerably shortened and the whole motion

is altogether more like that given by the "irrotational" solution ; in fact, at a distance from the sphere it is very similar to that which would be produced by the motion of a pear-shaped figure formed by the sphere and the fluid which is moving along with it. This is the highest velocity for which stream-lines could be mapped : photographs were indeed taken with velocities up to twice this value, but the lines were too faint to be measured. They do not indicate any important change in the form of the stream-lines.

The motion shown in Photo F (Pl. IX.) is altogether different from the others and was obtained with a sphere moving in water at the rate of ·074 cm. per sec. giving $Va/\nu = 7 \cdot 1$. This is the lowest velocity for which photographs could be obtained in water ; at lower velocities the motion is masked by irregular currents in the water due to temperature and other effects. The peculiar form of the stream-lines in this diagram may be due to some such effect, but the regularity with which the spreading out of the stream-lines behind the sphere appeared in a large number of different photographs, seemed to suggest that it may be due to some kind of instability appearing at this velocity.

It will be noticed that even at the highest velocity of fig. 8 we do not get the irregular eddying motion which has been observed in experiments in air and water channels. This may be due to the comparatively small values of the velocity employed in the present experiments, the eddies being due to an instability of the motion which only appears at values of the velocity beyond the highest used in these experiments ; it is also possible that the turbulence of the stream of air or water in the channel may affect the motion.

If, however, instead of a sphere we take a flat plate with its plane perpendicular to the direction of motion, eddies are formed and are shown very distinctly in the photographs, of which two are reproduced in G & H (Pl. IX.). In glycerine, the motion is very similar to that produced by the sphere under the same circumstances: in fact, the motion at low velocities is, except in the immediate neighbourhood of a moving body, practically independent of its shape. As the velocity changes beyond the critical value, the stream-lines change in very much the same way as for the sphere. Photo G for a velocity ·2 cm per sec. is of the same type as C, but beyond this value the development of the motion is very different. Photo H shows the motion for a velocity of ·59 cm. per sec., and it will be seen that we have here a full development of eddying motion. The "wake" is

separated from the rest of the fluid by a number of eddies for which the stream-lines are closed curves around a point of zero velocity. These eddies are in some respects similar to the vortices whose motion is worked out in the irrotational theory, and the dynamical effects must also be similar, as the very remarkable calculation of the resistance to the motion of plates and cylinders made by Kármán shows. A close study of the photograph shows, however, that there is a very great difference between the eddies and true " vortices," for in the eddies the central part of the liquid moves more or less as a solid body, the velocity diminishing towards the centre of the eddy where there is always a point of zero velocity, whereas in a vortex the velocity is inversely proportional to the distance from the centre, becoming infinite at that point. It is hoped by further experiments to trace out the gradual development of the eddies and the way in which they die away.

We may now proceed to compare the above results with those obtained by solving the equations of motion, and it will be convenient to begin with the results for very low velocities given in figs. 2 and 3. It was pointed out on p. 535 that these cannot be directly compared with Stokes's result owing to the influence of the outer boundary. The motion of a sphere inside a cylinder has been solved by Ladenburg [*], and the solution for a rectangular vessel might be obtained by the method of images developed by Lorentz [†]. The solutions obtained are, however, so very complicated that the numerical computation of the stream-lines would be exceedingly laborious, and for the same reason it would be impossible to use the solutions as a base of further approximation for higher velocities.

A very simple solution may, however, be obtained for the case of a sphere moving in the fluid contained in a concentric sphere, and the solution will apply with sufficient approximation to the case of a sphere moving at the centre of a cubical vessel which is represented in fig. 3.

The equations of motion with the inertia terms omitted and in the absence of impressed forces may be written :—

$$\frac{\partial u}{\partial t} = -\frac{1}{\rho}\frac{\partial p}{\partial x} + \nu \nabla^2 u,$$

with two similar equations for v and w.

If we now introduce the Stokes's stream function ψ defined

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* Ladenburg, *loc. cit.*
† Lorentz, *Abhandlungen*, i. p. 39.

by (2) and change to polar coordinates, the equations reduce to

$$D\left(D - \frac{1}{\nu}\frac{\partial}{\partial t}\right)\psi = 0 . \quad \ldots \quad (3)$$

where D is the operator

$$\frac{\partial}{\partial r^2} + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\operatorname{cosec}\theta \frac{\partial}{\partial \theta}\right),$$

for steady motion the equation reduces to

$$D^2\psi = 0 \quad \ldots \quad \ldots \quad (4)$$

The boundary conditions require that the velocity should be zero at the surface of the outer sphere and equal to V at the surface of the inner sphere. If a and b be the inner and outer radii respectively, these give :—

At $r=a$,

$$\frac{\partial\psi}{\partial\theta} = Va^2 \sin\theta\cos\theta, \quad \frac{\partial\psi}{\partial r} = Va \sin^2\theta \quad . \quad . \quad (5)$$

At $r=b$,
$$\psi = 0, \quad \frac{\partial\psi}{\partial r} = 0.$$

Let us assume $\psi = \left(\dfrac{A}{r} + Br + Cr^2 + Dr^4\right)\sin^2\theta$; this value satisfies (4) for all values of the constants A, B, C, D, and on substitution in (5) we get four equations to determine A, B, C, and D. In order to get a solution to compare with the case of a sphere in a cubical vessel given in fig. 3, we put $a=1$, $b=5\cdot7$, making the diameter of the sphere the same as the edge of the cube, and we then obtain $A = -\cdot413$, $B = 1\cdot237$, $C = -\cdot325$, $D = \cdot00339$, and the stream function is given by

$$\psi = \left(-\frac{\cdot413}{r} + 1\cdot237r - \cdot325r^2 + \cdot00339r^4\right) V \sin^2\theta. \quad (6)$$

The stream-lines given by this equation have been plotted out and are shown in fig. 9 and it will be seen that they agree very closely with the experimentally determined lines of fig. 3. A test of the agreement is given by the position of the point of zero velocity. This may be obtained from the formula by putting $\dfrac{\partial\psi}{\partial\nu} = 0$, and we thus get $r = 5\cdot6$, while the value measured on the diagram is $r = 5\cdot2$. Also if the diagram be compared with that of fig. 2 which represents motion in the rectangular trough it will be seen

that there is no very great difference between the values of the velocities in the neighbourhood of the sphere, so that the above solution may be regarded as an *approximate* representation of the motion of a sphere in an elongated vessel, the approximation being fairly close in the neighbourhood of the sphere.

Fig. 9.
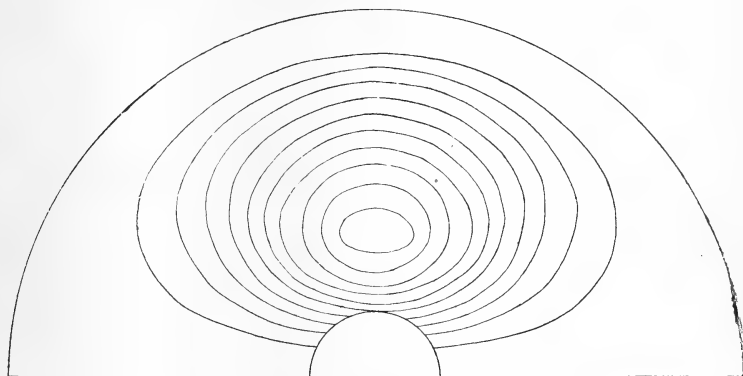
Sphere in sphere, $Va/\nu = 0$ (Theoretical).

Taking the solution obtained above as a base, we shall now attempt to obtain a second approximation in which the terms containing the second power of the velocity are partly taken into account.

Returning to the general equations of motion (1) and writing them in terms of cylindrical coordinates z, ϖ (symmetry about axis of z), we get for steady motion and no impressed forces the two equations

$$u\frac{\partial u}{\partial \varpi} + w\frac{\partial u}{\partial z} = \frac{\partial p}{\partial \varpi} + \nu\left(\nabla^2 u - \frac{u}{\varpi^2}\right),$$

$$u\frac{\partial w}{\partial \varpi} + w\frac{\partial w}{\partial z} = \frac{\partial p}{\partial z} + \nu\nabla^2 w.$$

Introducing the operator D defined above, these may be written

$$\frac{\partial p}{\partial z} = u\frac{\partial w}{\partial z} + w\frac{\partial w}{\partial z} + \frac{1}{\varpi}\frac{\partial}{\partial \varpi}(\nu D\psi),$$

$$\frac{\partial p}{\partial \varpi} = u\frac{\partial u}{\partial \varpi} + w\frac{\partial u}{\partial z} + \frac{1}{\varpi}\frac{\partial}{\partial z}(\nu D\psi).$$

Eliminating p by differentiation, we get

$$\nu D^2\psi = \left(u\frac{\partial}{\partial \varpi} + w\frac{\partial}{\partial z} - \frac{2u}{\varpi} \right) D\psi.$$

Denoting, for brevity, the operator on the right-hand side by ϑ, this becomes :—

$$\nu D^2\psi = \vartheta D\psi. \quad \ldots \quad \ldots \quad (7)$$

We have to solve this equation subject to boundary conditions of type (5).

Let $\psi = \psi_0 + \psi_1$, where ψ_0 is the solution for infinitely small velocities, and ψ_1 is to be looked upon as a correcting term which is small compared with ψ_0.

Substituting we have

$$\nu D^2\psi_0 + \nu D^2\psi_1 = \vartheta D\psi_0 + \vartheta D\psi_1. \quad \ldots \quad (8)$$

Now since ψ_0 is a solution of (4) $\nu D^2\psi_0 = 0$ and $\vartheta D\psi_1$ is of the third power of the velocity and may therefore be neglected. Further in the term $\vartheta D\psi_0$ we may neglect ψ_1 (occurring in the operator ϑ) as compared with ψ_0, so that $\vartheta D\psi_0$ contains ψ_0 alone and is therefore a known function of the coordinates. The equation thus becomes

$$\nu D^2\psi_1 = \vartheta D\psi_0. \quad \ldots \quad \ldots \quad (9)$$

and is a differential equation to determine ψ_1.

Now let $\psi_0 = \phi_0(r)\sin^2\theta$, $\psi_1 = \phi_1(r)\sin^2\theta\cos\theta$, where $\psi_0(r)$ is to be determined so that ψ_0 satisfies the boundary conditions and $\phi_1(r)$ is as yet undetermined.

Now $D^2\phi_1(r)\sin^2\theta\cos\theta =$

$$\left(\phi_1^{iv}(r) - \frac{12\phi_1''(r)}{r^2} + 24\frac{\phi_1'(r)}{r^3} \right)\sin^2\theta\cos\theta,$$

and $\vartheta D\phi_0(r)\sin^2\theta =$

$$\frac{2\phi_0(r)}{r^2}\left(\phi_0'''(r) - \frac{2\phi_0''(r)}{r} - \frac{2\phi_0'(r)}{r^2} + \frac{8\phi_0(r)}{r^3} \right)\sin^2\theta\cos\theta.$$

The term $\sin^2\theta\cos\theta$ thus divides out of (9) which becomes

$$\phi_1^{iv}(r) - \frac{12\phi''(r)}{r^2} + \frac{24\phi'(r)}{r^2}$$

$$= \frac{2\phi_0(r)}{\nu r^2}\left[\phi_0'''(r) - \frac{2\phi_0''(r)}{r} - \frac{2\phi_0'(r)}{r^2} + \frac{8\phi_0(r)}{r^3} \right]. \quad (10)$$

This is a differential equation of the fourth order to

determine $\phi_1(r)$, and the solution will contain four constants which may be adjusted so as to satisfy four boundary conditions such as (5).

If desired the process of approximation may be carried still further so as to include terms of the third degree in the velocity. To do this we must first substitute the value of $\phi_1(r) \sin^2 \theta \cos \theta$ in the operator $\mathfrak{S}$ in the first term on the right-hand side of (9). If now $\phi_1(r) \sin^2 \theta \cos \theta$ be substituted in the last term $\mathfrak{S} D \psi_1$ which was previously neglected, the resulting expression contains terms in $\sin^2 \theta$, $\sin^2 \theta \cos \theta$, and $\sin^4 \theta \cos \theta$, and hence by adding to the previous value of ψ a term of the form $\phi_2(r) [a \sin^2 \theta + b \sin^2 \theta \cos \theta + c^4 \sin^4 \theta \cos \theta]$ and suitably choosing the values of the numerical constants a, b, c, an equation giving $\phi_2(r)$ in terms of $\phi_0(r)$ and $\phi_1(r)$ may be obtained, and the approximation is thus corrected so as to include the terms of the third power in the velocity.

In applying the above solutions to actual cases for comparison with experimental results, certain difficulties are met with which are connected with the validity of Stokes's solution and are perhaps best dealt with here.

Reverting to the case of a sphere moving in an unbounded fluid, Stokes's solution may be written

$$\psi = \frac{3}{4} \mathrm{V} a r \left(1 - \frac{1}{3} \frac{a^2}{r^2}\right) \sin^2 \theta.$$

At a great distance from the sphere this becomes

$$\psi = \frac{3}{4} \mathrm{V} a r \sin^2 \theta,$$

and the corresponding velocities will be

$$\mathrm{R} = \frac{1}{r^2 \sin \theta} \frac{\partial \psi}{\partial \theta} = \frac{3}{2} \mathrm{V} \frac{a}{r} \cos \theta,$$

$$\Theta = - \frac{1}{r \sin \theta} \frac{\partial \psi}{\partial r} = - \frac{3}{4} \frac{\mathrm{V} a}{r} \sin \theta.$$

The velocity in the direction of motion of the sphere is

$$\frac{3}{2} \frac{\mathrm{V} a}{r} (\cos^2 \theta + \tfrac{1}{2} \sin^2 \theta).$$

The total momentum of the fluid in the direction of motion of the sphere is obtained by integrating this over the whole

of space outside the sphere, and its value is

$$\frac{3}{2}\,\mathrm{V}a\int_{r=a}^{r=\infty}\int_{\theta=0}^{\theta=2\pi}\int_{\phi=0}^{\phi=2\pi} r(\cos^2\theta + \tfrac{1}{2}\sin^2\theta)\,dr\,d\theta\,d\phi$$
$$=\frac{3}{2}\,\mathrm{V}a\frac{3\pi^2}{2}\Big[r^2\Big]_{r=a}^{r=\infty}.$$

This is evidently infinite even when V is infinitely small : now this momentum is produced by the force which acts on the sphere maintaining its velocity against the resistance of the fluid ; and since this force is proportional to the velocity and hence infinitely small, it must have acted for a time which is of the second order of infinite quantities. For the solution to be valid the sphere must therefore have moved from infinity with the same infinitely small velocity, otherwise the motion is not steady and equation (4) does not apply.

Now it is evident that if the velocity is not infinitely small, steady motion cannot be established, even when the sphere starts from infinity, as the time during which the force acts is now infinite of the first order only. The precise extent of the departure from steady motion may be found by considering the case of a sphere starting from rest and proceeding with a small uniform velocity. This case has been solved by Bassett (Hydrodynamics, ii. p. 286), whose solution may be written

$$\psi = \psi_0 - \frac{3\mathrm{V}a\sin^2\theta}{r\sqrt{\pi}}\int_0^{\frac{r-a}{2\sqrt{\nu t}}}\Big[2\lambda^2\nu t + 2a\lambda\sqrt{\nu t/\pi} + \tfrac{1}{2}(a^2 - r^2)\Big]e^{-\lambda^2}d\lambda.$$

When r is small and t great the second term vanishes and the motion is the same as in the steady state, but when r is large the integral does not vanish even for very large values of t ; for the motion is only steady when $\dfrac{r}{\sqrt{t}}$ vanishes, and hence at points very distant from the sphere the motion never becomes steady. The conditions are not very much improved when the fluid is confined by an outer boundary, so that only small values of r need be considered, for the time during which motion is possible without completely altering the boundary conditions diminishes in the same proportion as the dimensions of the boundary. The only case where a steady motion is experimentally realisable is when the outer boundary is a tube or elongated vessel, for then the motion of the fluid is confined to the portion of the tube in the neighbourhood of the moving sphere, and

the boundary conditions are not seriously altered by a considerable movement of the sphere. Now we have seen that the motion given by the sphere in sphere solution of (6) also represents very closely the motion in an elongated rectangular vessel, and a second order approximation based on this solution may be expected to show the way in which the motion in this case alters with increasing velocity, even if it does not give an exact representation of it.

There is, however, another cause which limits the validity of Stokes's solution at a great distance from the sphere, which has been pointed out by Oseen and Lamb [*]. To get really steady motion it is necessary to consider the sphere as at rest in an infinite stream of fluid, or to consider the origin as moving with the sphere. In either case the velocity of the fluid relative to the origin has a fixed constant value at infinity. Now the validity of Stokes's solution depends on the possibility of neglecting terms of the form $u\dfrac{\partial u}{\partial x}$ compared with terms of the form $\nu\dfrac{\partial^2 u}{\partial x^2}$. In this case $\dfrac{\partial u}{\partial x}$ and $\dfrac{\partial^2 u}{\partial x^2}$ diminish indefinitely as the distance from the origin increases while u remains constant, hence however small u may be, it is impossible to neglect $u\dfrac{\partial u}{\partial x}$ when r is great.

Oseen has obtained a solution in which this fact is taken into account, but as it only differs from the ordinary solution at considerable distances from the sphere, it is not easy to test it experimentally, nor does it seem possible to base a second approximation on it.

If, instead of referring the motion to an origin that moves with the sphere, we refer it to a fixed origin, coinciding at any instant with the centre of the sphere, the velocity of the fluid far from the origin will be zero, and hence the term $u\dfrac{\partial u}{\partial x}$ can be neglected over the whole field. On the other hand, the motion is not strictly steady except when quantities of the second order are neglected. For let the sphere be moving with velocity V and let ξ be the distance of its centre from a fixed point, then if ψ be the stream function,

$$\psi = f(z + \xi, \varpi, t),$$
$$\frac{d\psi}{dt} = \frac{\partial f}{\partial t} + V\frac{\partial f}{\partial \xi}.$$

The last term is of the second order in the velocity, and when these are neglected $\dfrac{d\psi}{dt} = 0$ when $\dfrac{\partial f}{\partial t} = 0$, so that the motion is steady with respect to both fixed and moving origins ; it is in fact immaterial which system we choose. When these terms are not neglected this is no longer the case, but if reference is made to fig. 2 it will be seen that in the immediate neighbourhood of the sphere the stream-lines are all parallel to the axis of z, and therefore $\dfrac{\partial f}{\partial \xi}$ is zero, and the second term is therefore nowhere very important, and the results obtained by referring the motion to a fixed origin may be expected to give a better representation of the results than if the origin is taken to move along with the sphere. This was in fact found to be the case, and the calculations being similar for both cases only those referred to a fixed origin are given below.

The solution for a sphere in a concentric sphere gives

$$\phi_0(r) = \frac{A}{r} + Br + Cr^2 + Dr^4.$$

Substituting in (10) we obtain

$$\phi_1^{\mathrm{iv}}(r) - \frac{12\phi_1''(r)}{r^2} + \frac{24\phi_1'(r)}{r^3} = \frac{12B}{\nu r^4}\left[\frac{A}{r} + Br + Cr^2 + Dr^4\right];$$

a particular solution of this is

$$\phi_1(r) = \frac{1}{\nu}\left[-\frac{AB}{2r} + \tfrac{1}{2}B^2r + \tfrac{1}{2}CBr^2 - \tfrac{1}{2}DBr^4\right],$$

and the complementary function is

$$\frac{l}{r^2} + mr^3 + nr^5 + p,$$

where l, m, n, and p are constants to be determined by the boundary conditions.

Thus the complete solution of equation (9) is

$$\psi = \left(\frac{A}{r} + Br + Cr^2 + Dr^4\right)V\sin^2\theta + \left[\frac{1}{2\nu}\left(-\frac{AB}{r} + B^2r\right.\right.$$
$$\left.\left. + BCr^2 - BDr^4\right) + \frac{l}{r^2} + mr^3 + nr^5 + p\right]V^2\sin^2\theta\cos\theta.$$

The boundary conditions to determine l, m, n, and p are

$$\phi_1(r) = \frac{\partial\phi_1(r)}{\partial r} = 0 \ \text{ at } \ r=a, \quad r=b.$$

For the case of an outer sphere of radius 5·7 we get on substituting for A, B, C, and D, and solving the boundary equations for l, m, n, p,

$$l = -\cdot0171, \quad p = -\cdot824, \quad m = \cdot0224, \quad n = \cdot000166.$$

To compare with the experimental result of fig. 4 the values of ψ have been calculated for $Va/\nu = 2$, and the resulting values of ψ are plotted in fig. 10. It will be seen on comparing the two diagrams that the theoretical solution is a

Fig. 10.
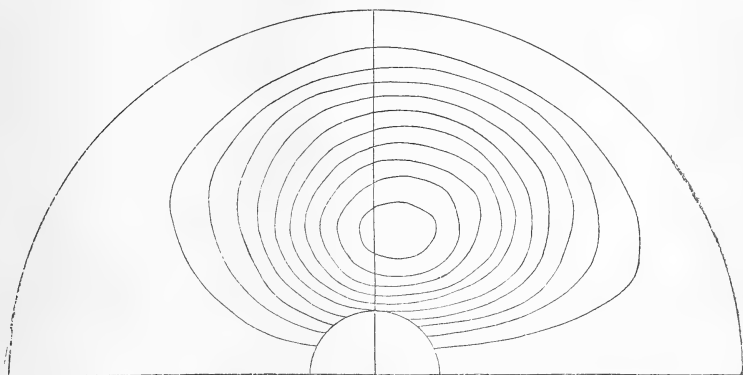
Sphere in sphere, $Va/\nu = 2$ (Theoretical).

very fair representation of the observed result. The second term containing $\sin^2\theta\cos\theta$ is unsymmetrical with respect to the median plane, and accounts for the backward trend of the stream-lines. A quantitative measure of the agreement between the two diagrams may be obtained by measuring the displacement of the point of zero velocity from the median line. In the theoretical diagram this is ·8 cm. and in the experimental ·9 cm. The approximate solution is not applicable to values of $\dfrac{Va}{\nu}$ much higher than 2, on attempting to apply it for a value of 3 it was found that the stream function became negative in portions of the field.

As has been already explained, the above solutions are only applicable to motion in elongated vessels, as steady motion is impossible in other cases. The equations of motion may, however, be solved in certain cases without the restriction to steady motion, and we may thus get a solution applicable to a sphere moving in an infinitely extended fluid. This can be done if we apply the method of approximation

given above to Stokes's solution of the motion of a spherical pendulum-bob given in his memoir of 1850.

When the motion is not steady equation (8) takes the form

$$D'\left(D\psi - \frac{1}{\nu}\frac{\partial\psi}{\partial t}\right) = \frac{1}{\nu}\vartheta D\psi. \quad . \quad . \quad . \quad (11)$$

Let us assume that the position and velocity of the sphere are exponential functions of the time and write, following Stokes,

$$V = ce^{\lambda^2\nu t}.$$

Then if we write $\psi_0 = ce^{\lambda^2\nu t}\phi_0(r)\sin^2\theta$,
where

$$\phi_0(r) = \tfrac{1}{2}a^2\left\{\left(1 + \frac{3}{\lambda a} + \frac{3}{\lambda^2 a^2}\right)\frac{a}{r} - \frac{3}{\lambda a}\left(1 + \frac{1}{\lambda r}\right)e^{-\lambda(r-a)}\right\}. \quad (12)$$

ψ_0 is the solution for infinitely small velocity and satisfies the left-hand side of (11) equated to zero.

As before let $\psi = \psi_0 + \psi_1$ be the solution of (11), then on substituting and neglecting third-order terms we get

$$D\left(D\psi_1 - \frac{1}{r}\frac{\partial\psi_1}{\partial t}\right) = \frac{1}{\nu}\vartheta D\psi_0, \quad . \quad . \quad . \quad (13)$$

the right-hand side being a function of ψ_0 only which may be written

$$\chi(r)\,ce^{2\lambda^2\nu t}\sin^2\theta\cos\theta,$$

$\chi(r)$ being a known function obtained by operating on $\phi_0(r)$.

To solve (13) we assume

$$\psi_1 = c^2 e^{\lambda_1^2\nu t}\,\phi_1(r)\sin^2\theta\cos\theta,$$

λ_1 and $\phi_1(r)$ being for the present undetermined.

Substituting in (13) we have

$$D\left\{\left(\phi_1''(r) - \frac{6}{r_2}\phi_1(r) - \lambda_1^2\phi_1(r)\right)e^{\lambda_1^2\nu t}\sin^2\theta\cos\theta\right\}$$
$$= \chi(r)e^{2\lambda^2\nu t}\sin^2\theta\cos\theta.$$

Let us denote the function in the brackets by $\xi(r)$, then the above equation becomes

$$D\{\xi(r)e^{\lambda_1^2\nu t}\sin^2\theta\cos\theta\} = \chi(r)e^{2\lambda^2\nu t}\sin^2\theta\cos\theta,$$

or

$$\left(\xi''r - \frac{6}{r^2}\xi r\right)e^{\lambda_1^2\nu t} = \chi(r)e^{2\lambda^2\nu t}. \quad . \quad . \quad . \quad (14)$$

This equation together with

$$\phi_1''(r) - \frac{6}{r^2}\phi_1(r) - \lambda_1^2\phi_1(r) = \xi(r)$$

serve to determine λ_1 and $\phi_1(r)$, the arbitrary constants being determined by the boundary conditions, and the problem is thus reduced to that of the solution of the two linear equations (14) and (15).

To solve (14) we must evidently have $\lambda_1 = \sqrt{2}\lambda$, and then the equation becomes

$$\xi''(r) - \frac{6}{r^2}\xi(r) = \chi(r).$$

A particular solution of the left-hand equated to zero is $\xi(r) = Br^3$, and hence the complete solution is

$$\xi = r^3\left[C + D\int\frac{dr}{r^6} + \int\frac{dr}{r^6}\int r^3\chi(r)dr \right]. \quad . \quad . \quad . \quad (16)$$

We have now to solve

$$\phi_1''(r) - \frac{6}{r^2}\phi_1(r) - 2\lambda^2\phi_1(r) = \xi(r).$$

The equation

$$\phi_1''(r) - \frac{6}{r^2}\phi_1(r) - 2\lambda^2\phi_1(r) = 0$$

is solved by

$$\phi_1(r) = e^{-\sqrt{2}\lambda r}\left(2\lambda^2 + 3\sqrt{2}\frac{\lambda}{r} + \frac{3}{r^2} \right);$$

if this be written $\zeta(r)$ for brevity, then the solution of the complete equation is

$$\phi_1(r) = \zeta(r)\left[E + F\int\frac{dr}{\zeta^2(r)} + \int\frac{dr}{\zeta^2(r)}\int\zeta(r)\xi(r)dr \right]. \quad . \quad (17)$$

The solution for ψ may now be written

$$\psi = ce^{\lambda^2 vt}\phi_0(r)\sin^2\theta + c^2 e^{2\lambda^2 vt}\phi_1(r)\sin^2\theta\cos\theta$$
$$= V\phi_0(r)\sin^2\theta + V^2\phi_1(r)\sin^2\theta\cos\theta. \quad . \quad . \quad (18)$$

In calculating this solution for particular cases the integrals occurring in the expressions for $\phi_1(r)$ are best evaluated by numerical methods. In order to reduce the labour of calculation, it is necessary to use an interpolation formula so as to be able to carry out the calculation with a small

number of tabulated values of $\chi(r)$. This function is of an exponential form except when r is small, and it was found that the usual interpolation formulæ (Newton and Gauss) did not give sufficiently accurate results, since, being based on Taylor's theorem, they fail when the successive differential coefficients do not diminish fairly rapidly. A very simple interpolation formula may, however, be based on the assumption that the functions are exponentials with slowly varying indices. Thus suppose a, b, are two consecutive values of the variable in the table, and $f(a)$, $f(b)$, the corresponding values of the function which is to be integrated, and let $a + h$ be the value of the variable in the step $a-b$, h varying continuously from 0 to $(b-a)$; then we may put

$$f(a+h) = f(a)e^{kh},$$

k being a different constant for each step in the table.

$$\therefore \quad \int f(a+h) = \frac{f(a)\,e^{kh}}{k},$$

hence

$$\int_a^b f(a+h) = \frac{f(b)-f(a)}{k},$$

and the index k is given by

$$k = \frac{1}{b-a}\log\frac{f(b)}{f(a)}.$$

The step $(b-a)$ is usually unity, and hence k is found at once by subtracting the logarithms of the two consecutive terms in the table, and the step of the integral is got by subtracting the two terms and dividing by k. The interpolation can thus be carried out without any very laborious computation.

The calculations have been carried out for two values of λ, namely $\lambda = \cdot09$ and $\lambda = 1$. The first represents a very slowly changing velocity and is not very different from the case of steady motion, while the latter value gives the case of very rapidly accelerated motion. The results obtained are given in the accompanying table showing the values of $\phi_0(r)$ and $\phi_1(r)$ for different values of r. The value of ψ at any point is obtained by substituting in (18).

In figs. 11 and 12 these values of ψ have been plotted out for $\lambda = 1$ and for two values of the velocity, one above and one below the critical value. It will be seen that the change

r.	$\lambda = \cdot 09$.		$\lambda = 1 \cdot 0$.	
	$\phi_0(r)$.	$\phi_1(r)$.	$\phi_0(r)$.	$\phi_1(r)$.
1·0	·5	·000	·500	·00
1·2	·73	·002	·670	·00051
1·4	·90	·0078	·780	·00146
1·6	1·02	·0129	·845	·00260
1·8	1·11	·0198	·900	·00336
2·0	1·18	·0277	·920	·00406
2·2	1·27	·0344	·935	·00474
2·4	1·36	·0398	·935	·00469
2·6	1·44	·0446	·925	·00439
2·8	1·52	·0490	·915	·00415
3·0	1·59	·0524	·900	·00406
4·0	1·815	·0586	·785	·00350
5·0	1·92	·0668	·670	·00300
6·0	1·96	·0624	·575	·00214
7·0	1·94	·0630	·495	·00152
8·0	1·90	·0630	·436	·00115
9·0	1·84	·0670	·389	·0008
10·0	1·76	·060	·350	
20·0	1·088	·058		
30·0	·73	·003		

Fig. 11.
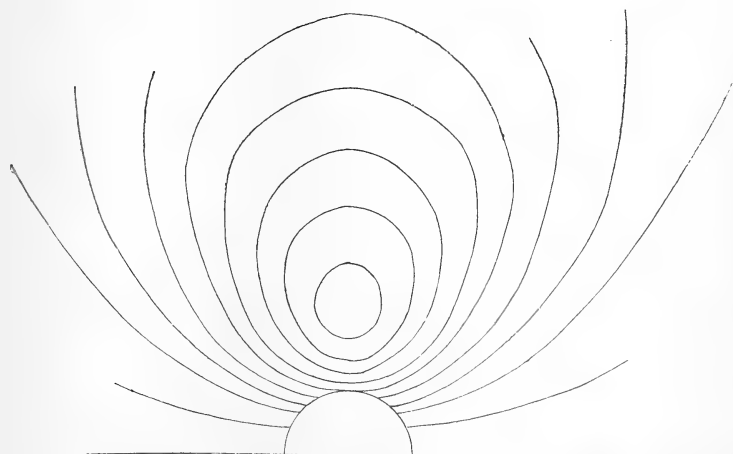
Accelerated motion of sphere, $\mathrm{V}a/\nu = 0$ (Theoretical).

in the form of the stream-lines is of a similar character to
that in the steady motion; with increasing velocity the
motion becomes unsymmetrical with respect to the median

plane, the velocity of the fluid increasing behind and diminishing in front of the moving sphere.

Fig. 12.
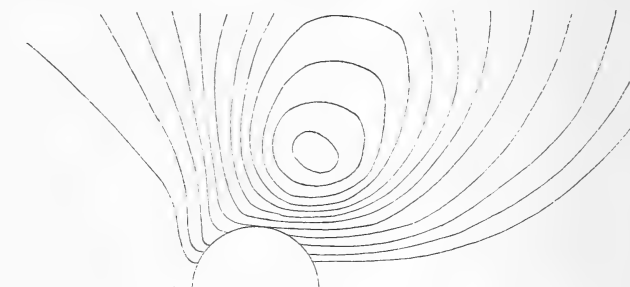
Accelerated motion of sphere $Va/\nu = 3$ (Theoretical).

The solutions thus obtained are of course only applicable to values of $\dfrac{Va}{\nu}$ slightly above the critical value ; the form of the stream-lines in figs. 7 and 8 seems to show that a solution for these cases may be obtained by starting with the discontinuous motion worked out by Kirchhoff and Rayleigh, and some encouraging results have been obtained which will be given in a later paper.

LVI. *Note on the Relative Dimensions of Molecules. By* A. O. RANKINE, *D.Sc., Fellow of and Assistant in the Department of Physics in University College, London**.

IT is well known that the knowledge of the viscosity of a gas makes it possible to calculate upon the kinetic theory the mean free path of the molecules, and hence their dimensions. According to Maxwell the relations are as follows :—

$$\eta = 0{\cdot}307\rho\lambda G, \quad \ldots \quad \ldots \quad \text{(i.)}$$

where η is the viscosity, ρ the density, λ the mean free path, and G the root mean square velocity of the gas molecules. The value of G is $\sqrt{\dfrac{3p}{\rho}}$, where p is the pressure of the gas.

Further, the equation

$$\lambda = \frac{1}{\sqrt{2}N\pi\sigma^2}, \quad \ldots \quad \ldots \quad \text{(ii.)}$$

where N is the number of molecules per unit volume and σ is the radius of the molecule. gives the connexion between the mean free path and the molecular radius.

As was pointed out by Sutherland[*], however, the calculation of σ by means of these two equations leads to inconsistencies, because the viscosity of a gas is not, in fact, proportional to the square root of the absolute temperature. Hence the value of σ so estimated becomes smaller and smaller as the temperature corresponding to the viscosity datum increases.

The modification in the theory introduced by Sutherland was to take into account the forces of attraction which the gaseous molecules exert upon one another ; and he showed that this involved that the mean free path was smaller than that estimated for forceless molecules in the ratio $1 : 1 + \dfrac{C}{T}$, where C is a constant and T is the absolute temperature.

Upon this basis Sutherland showed that the viscosity of a gas, instead of being proportional to the square root of the absolute temperature, was proportional to $\dfrac{T^{\frac{1}{2}}}{1 + \dfrac{C}{T}}$. This modified theory has been found to correspond with experiment very well, at any rate much more accurately than the simple theory.

In applying these results to the calculation of molecular dimensions we have, according to Sutherland, to diminish the molecular radius as estimated from the simple theory in the proportion $\left(1 + \dfrac{C}{T}\right)^{\frac{1}{2}} : 1$, in order to obtain the true radius, for the molecular attractions make the molecules behave from the point of view of frequency of collision as though they were larger than they are in reality.

For this purpose, therefore, we require to know not merely the viscosity of a gas at one temperature, but also the variation with temperature, so that the constant C can be found.

The author has recently made such measurements for a considerable number of gases, and the molecular dimensions deduced therefrom exhibit some points of interest. The gases in question are three members of the group of inert gases, viz. argon, krypton, and xenon, and the three corresponding members of the halogen group, viz. chlorine, bromine, and

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[*] Sutherland, Phil. Mag. vol. xxxvi. p. 507 (1893).

iodine.　These two sets of gases are adjacent in pairs in the Periodic Table.

The molecular radii of these gases, calculated in the way above indicated, are shown in the following table:—

TABLE I.

Gas.	Molecular radius $\times 10^8$ cm.	Gas.	Molecular radius $\times 10^8$ cm.	Ratio.
Chlorine	1·60	Argon	1·28	1·25
Bromine	1·71	Krypton ...	1·38	1·24
Iodine	1 88	Xenon	1·53	1·23

The figures reveal the notable fact that the dimensions of each corresponding pair of gases in the two groups are in constant proportion, the numbers in the last column being practically equal.　In other words, we may say that the radius of the molecule of a halogen gas is 1·24 times as great as the molecular radius of the corresponding inert gas. This statement is, of course, based upon the assumption that all the molecules are spherical.

The cube of 1·24 is 1·91, or practically 2.　This means that the halogen molecules have practically twice the volume of the corresponding inert molecules.

The molecular masses are also approximately in the proportion of 2 : 1, for the atomic masses of corresponding gases are nearly equal, the halogens being diatomic and the inert gases monatomic.　We should thus expect the *densities of the molecules* of, for example, iodine and xenon to be equal, and a similar equality for the other pairs.　This is set forth in detail in the following table.

TABLE II.

Pair of Gases.	Ratio of Molecular Masses (from molecular weights).	Ratio of Molecular Densities (from viscosities).
Chlorine : Argon ...	1·78	0·93
Bromine : Krypton.	1·93	1·01
Iodine : Xenon......	1·95	1·02

It is, perhaps, worthy of note that the case where the ratio of densities differs most from unity is that where argon is involved, and that argon has, from the point of view of the periodic arrangement of the elements, an abnormally high atomic weight, the effect of which is to give the above-mentioned ratio a low value.

Another point of interest in connexion with the molecular dimensions of these two groups of gases may be based upon the interpretation of Sutherland's constant C previously referred to. This constant is a measure of what Sutherland called " the potential energy of two molecules in contact with one another," but which would be better defined as " the work done against attractive forces in separating to an infinite distance two molecules originally in contact."

The following table shows the relation which exists between these quantities of work for the pairs of gases with which we have previously dealt.

TABLE III.

Pair of Gases.	Values of C.		Ratio $\dfrac{C_{(halogen)}}{C_{(inert)}}$
Chlorine : Argon ...	325,	142	2·3
Bromine : Krypton.	460,	188	2·4
Iodine : Xenon	590,	252	. 2·3

The numbers in the last column are constant to an extent certainly within the accuracy with which the values of C are known. We may therefore say that the work done in separating to a great distance two molecules of a halogen gas originally in contact is 2·3 times as great as for two molecules of the corresponding inert gas.

The attempt to go further and investigate the law of force upon the basis of these figures has been made by the author, but has been found to lead to inconsistencies. One is driven to the conclusion that a single law of force depending in a definite way on mass and distance only cannot apply to molecules differing widely in internal constitution.

LVII. *On the Precision Measurement of Air Velocity by means of the Linear Hot-Wire Anemometer. By* Louis Vessot King, *B.A. (Cantab.), Assistant Professor of Physics, McGill University, Montreal* *.

[Plate X.]

Section 1. Details of Construction of the Linear Hot-Wire Anemometer.

IN a paper recently published by the writer †, the theory of the convection of heat from small cylinders cooled by a stream of fluid was extensively studied, the results compared with experiment and applied to the development of a precision anemometer intended to be of service in studying complex problems of gas-flow. The special type of instrument referred to may be called a " linear anemometer " in contradistinction to several forms of integrating instruments which have already been described ‡. Detailed specifications are given in the memoir referred to for the construction of this instrument. Use is made of the Kelvin Bridge

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* Communicated by the Author.

† Read before the Royal Society of Canada, May 28, 1913. " On the Convection of Heat from Small Cylinders in a Stream of Fluid : Determination of the Convection Constants of Small Platinum Wires, with Applications to Hot-Wire Anemometry," Phil. Trans. Roy. Soc. London, vol. ccxiv. A. pp. 373–432, 1914 ; abstract in the Proceedings of the Roy. Soc. A. vol. xc. 1914, pp. 563–570.

‡ Preliminary experiments on the use of a platinum wire heated by an electric current for the measurement of wind-velocity were carried out by G. A. Shakespear, at Birmingham, as early as 1902, but were discontinued for lack of facilities in the erection of a suitable whirling table for the calibration of the wires. Electrical anemometry was independently suggested by A. E. Kennelly in 1909 (A. E. Kennelly, C. A. Wright, and J. S. Van Bylevelt, Trans. A. I. E. E. 28, pp. 363–397, June 1909), and although the actual application to anemometry appears to have been made as early as 1911, the results have only recently been published (A. E. Kennelly and H. S. Sanborn, Proc. of the American Phil. Soc. 8, pp. 55–77, April 24, 1914). Electrical anemometry was also developed independently by U. Bordoni (paper read before the Società Italiana per il Progresso delle Scienze, Oct. 13, 1911 ; published in the " Nuovo Cimento," series 6, vol. iii. pp. 241–283, April 1912 ; see also ' Electrician,' 70, p. 278, Nov. 22, 1912), and by J. T. Morris (paper read at the British Association, Dundee, Sept. 27, 1912 ; published in the ' Engineer,' Sept. 27, 1912, the ' Electrician,' Oct. 4, 1912, p. 1056, and Nov. 22, 1912, p. 278). A form of integrating hot-wire anemometer has also been described by H. Gerdien (*Ber. der Deutschen Phys. Ges.*, Heft 20, 1913). The use of a hot-wire anemometer in the measurement of non-turbulent air currents is described by C. Retschy in a series of short papers published in *Der Motorwagen*, vol. xv. March–July, 1912.

connexions shown in fig. 1; the ratio-coils are adjusted so that $a/b = \alpha/\beta$, in which case a fundamental property of this arrangement is that when a balance is obtained on the

Fig. 1.

Diagram of Kelvin Bridge Connexions employed in Precision Hot-Wire Anemometry.
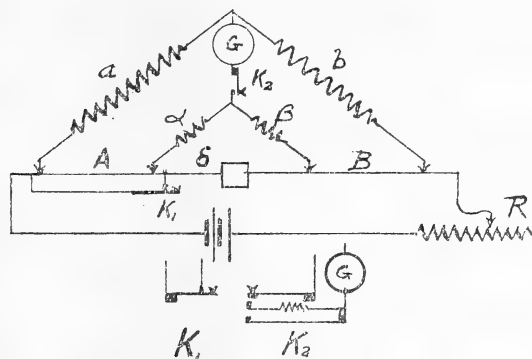
galvanometer, $A/B = a/b = \alpha/\beta$ independently of all connect-ing- or contact-resistances. The resistances A and B refer respectively to the resistance of the anemometer-wire between potential terminals permanently fused to the wire and to that of a manganin resistance. The resistances a and b were made equal and about 500 ohms, while α and β were adjusted to equality at about 250 ohms. In order to protect the anemometer-wire from accidentally burning out, a key K_1 was inserted by means of which it was always short-circuited except when observations were actually being taken; a double-contact key K_2 was inserted in the galvanometer circuit in such a way that contact was first made through a high resistance in the preliminary adjustments; it was also found convenient to connect the galvanometer through an ad-justable shunt. The resistance B was constructed of No. 23 B. and S. gauge manganin wire wound non-inductively on an asbestos frame so as to dissipate a maximum amount of heat; its resistance as measured between potential terminals soldered to the wire was adjusted to about four times that of the anemometer-wire at room temperature. By means of a fine-adjustment rheostat R, the current in the anemometer-wire can be adjusted until a balance is obtained on the galvano-meter. It is advisable that the rheostat be always readjusted to the position of minimum current to avoid overheating the wire should the velocity of air-flow suddenly diminish; this

may easily be accomplished by means of a spring control. In taking a measurement of velocity the key K_1 is pressed down and the current as read by the ammeter slowly increased until on pressing down the key K_2 a balance is obtained on the galvanometer. From the reading of the current i the velocity V may readily be obtained from a calibration curve corresponding to the formula

$$i^2 = i_0{}^2 + k \sqrt{V}, \quad \cdots \quad (1)$$

or from a conversion-table connecting i and V calculated from the above expression.

The ammeter employed by the writer was a Weston direct-current instrument of range 2 amperes ; the scale was equally graduated over this range, each division representing $0 \cdot 02$ ampere ; by estimation the current could be read to $0 \cdot 002$ ampere. If the conditions of air-flow are sufficiently steady and it is required to resolve small velocity differences, the use of a Weston Laboratory Standard ammeter is recommended ; the scale covers a range of $1 \cdot 5$ amperes and is uniformly graduated directly to $0 \cdot 01$ ampere ; by means of a diagonal scale it is possible to subdivide each division directly into fifths and by estimation to twentieths, so that it is possible to read the current to $0 \cdot 0005$ ampere.

The galvanometer employed was a Weston portable instrument with jewel-bearings, of resistance 277 ohms and capable of detecting a current of about 10^{-6} ampere ; this degree of sensitivity is, in fact, ten times more than is necessary. When employed in connexion with hot-wire anemometry the constants of damping are very important in determining the rapidity with which observations can be made. It was found that equally sensitive galvanometers varied within wide limits in this respect.

A convenient form of fork suitable for holding in position the anemometer-wires, and offering a minimum of disturbance to the flow of air in its neighbourhood, is illustrated in fig. 2. Fastened to a block of ebonite are the two arms of the fork consisting of steel strips about 5 mm. in width. At the end of each is soldered a small brass block drilled to receive two fine needles fastened about 1 cm. apart. Threaded through the eyes of these two needles is a 3-mil platinum wire having its extremities firmly clamped in the brass block just mentioned. The ends of the anemometer-wire are threaded through these two loops and secured in position by being twisted a couple of turns around the wire ; the fundamental property of the Kelvin Double Bridge already referred to

only requires the electrical contact at these points to be moderately good. The tension in the wire is adjusted by a fine silk thread carried down from each of the brass blocks to an adjustable screw in the centre of the ebonite block;

Fig. 2.

Details of Fork for holding Anemometer-Wires and Potential Terminals.
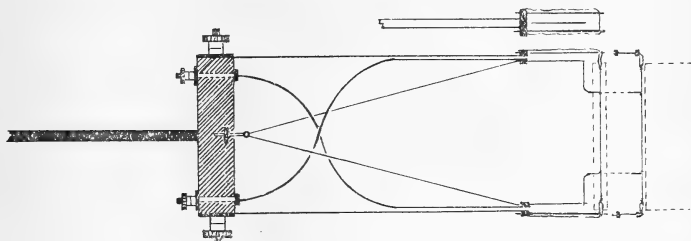
[The wire is shown in position over an end of a channel of rectangular cross-section, and illustrates the guard-ring effect obtained by the use of potential terminals fused to the wire.]

this thread is also effective in preventing lateral vibrations of the fork. Carried up from each end of the ebonite block are two thin steel strips crossing each other to the opposite arms of the fork, insulated from each other and also from the fork by means of thin mica strip. These steel strips, which are held in position along the arms of the fork by two lashings of fine waxed silk cord, serve to brace the fork and at the same time serve as potential leads ; at each end is soldered a small brass block drilled to hold a fine needle at the extremity of which is soldered a short length of 6-mil platinum wire. To these are soldered one extremity of the 1-mil platinum potential terminals, the other being *fused* to the anemometer-wire; this is most easily accomplished by connecting the wire to the bridge connexions and adjusting the current until it is at a bright red heat ; the potential wires are then brought to the required position and wound twice around the anemometer-wire ; by applying a slight tension while this is being done, a satisfactory fused contact will be effected. The free end should then be broken or cut off close to the anemometer-wire, so as to diminish the cooling effect of the potential leads. The heating to which the wire is subjected during this operation serves to anneal it sufficiently well for permanent use.

In the course of experiments by the writer on the flow of air between parallel planes, considerable experience has been acquired as to the most suitable method of employing the

linear anemometer in precision measurements of air-velocity. In the following sections are set out in greater detail directions as to the most efficient method of using the instrument and data now available as to the resolving power, upper and lower limits of correct velocity registration, life of wires, sources of error, &c., which may be of use to experimenters wishing to employ the linear anemometer in aerotechnical investigations.

Section 2. On the Selection and Calibration of Anemometer-Wires.

Platinum wire $2\frac{1}{2}$ or 3 mils in diameter is found to be most suitable for the purposes of hot-wire anemometry. The metal should be as pure as possible as judged from a determination of the specific resistance and temperature coefficient. The wire employed in platinum thermometry is especially suited to the purpose in that its electrical constants are usually specified with great accuracy. The wire should be drawn down to $2\frac{1}{2}$ or 3 mils, and if found to be satisfactory on microscopic examination, a considerable length should be reserved for the purposes of anemometry ; if possible the final diamond die employed should be reserved solely for drawing down anemometer-wires. The wire having been mounted and annealed in the manner already described and the potential terminals fused in position, the manganin resistance should be set to the value previously determined as that to which the anemometer must be heated by the electric current in order to attain the temperature best suited to the type of velocity measurement to be undertaken. For most purposes a temperature which corresponds to a dull red appearance of the wire is most suitable. Wires may be set roughly to the same temperatures by adjusting the manganin resistance so that a balance is obtained for the same current when the anemometer-wire is in stagnant air, carefully protected from draughts. The potential terminals are generally fused to the anemometer-wire at a distance of 2·5 cm. apart, although for some purposes the writer has worked with a distance as small as 1 cm. The distance between potential terminals could be made very much less if the wire is calibrated directly, though at a considerable loss in galvanometer sensitivity ; a sensitivity of 10^{-6} ampere would probably be sufficient for use with a wire of $2\frac{1}{2}$ mm. between potential terminals ; as the velocity measured is practically that over this distance, it is seen that velocities can approximately be measured at a point with a minimum disturbance of flow.

It is preferable to calibrate the wire directly by means of a rotating arm, the velocity being corrected for "swirl" in the manner already described [*]. Wires are usually calibrated by the writer over the range $V = 60$ to 800 cm./sec., enabling the constants of the formula

$$i^2 = i_0{}^2 + k\sqrt{V} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

to be determined; experiments are discussed below showing that this formula may with fair accuracy be employed in the determination of velocity very considerably above and below these limits. For precision work a series of about ten determinations of current and velocity should be taken, and the points $y = i^2$ and $x = \sqrt{V}$ plotted on accurate section paper in order to eliminate possible gross errors or accidental mistakes of reading. The line of closest fit to this series of points should then be determined by calculation; the scale is altered by multiplying y or x by a suitable power of ten, so that these coordinates are expressed by numbers of the same magnitude. Under these conditions the line of closest fit may conveniently be taken to be the major axis of inertia of the system of points regarded as masses of equal weights. If there are n points, the inclination of this line, whose equation may be written $y = y_0 + x \tan \theta$, is easily seen to be given by the formula

$$\tan 2\theta = \frac{2\left[\Sigma(xy)/n - \bar{x}\bar{y}\right]}{\Sigma(x^2 - y^2)/n - (\bar{x}^2 - \bar{y}^2)}, \quad . \quad . \quad . \quad (2)$$

$\bar{x}$ and $\bar{y}$ being the coordinates of the centre of gravity given by $\bar{x} = \Sigma(x)/n$, $\bar{y} = \Sigma(y)/n$. From this formula we find $\tan \theta$ and y_0, from the formula $y_0 = \bar{y} - \bar{x} \tan \theta$; hence reducing back to the original scale we obtain $i_0{}^2$ and k. The calculation is somewhat facilitated by taking $n = 10$. The agreement of two independent determinations of the calibration constants computed in this way is well illustrated in the case of wire 17, Table II.

While velocities corresponding to an observed value of i may easily be obtained from the calibration curve corresponding to formula (1), a considerable saving of time can be effected if more than 100 current observations have to be reduced to velocities by calculating out a conversion-table corresponding to the formula

$$V = k^{-2}(i^2 - i_0{}^2)^2, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

at intervals of $0\cdot01$ ampere over the range required. The

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[*] Phil. Trans. paper, pp. 388, 428; in the sequel this paper will be referred to as reference (1).

calculations are very quickly carried out by the use of a table of squares, Crelle's Multiplication Tables and a calculating machine ; a 150-entry table can easily be computed in an hour. Calculations should be entered with one significant figure more than is to be employed finally, and first differences should be tabulated for convenience in interpolation and as a check on the accuracy of the work.

If the anemometer is to be employed in the measurement of very low velocities (of the order of 10 cm./sec. or less), the disturbing effect of the free convection current set up by the heated wire may become sensible. From data derived in the course of the experiments by the writer already referred to, the " effective velocity " of the free convection current set up by a 3-mil wire at 1000° C. is estimated at about 15 cm./sec., is only reduced to about 8 cm./sec. at 200° C., and does not diminish materially with the diameter of the wire*. The effect of the free convection current on the determination of velocity from formula (1) at low velocities would demand a separate investigation. Some information on this point can be derived from the experiment described under fig. 3, in which the distribution of the flow of air into a slit in a plane is measured and compared with the distribution calculated from theory. The evidence there discussed points to the fact that the anemometer registers velocities as low as 15 cm./sec. with an accuracy of about ten per cent. For use in low-velocity measurement it is, however, more satisfactory to calibrate the anemometer under such conditions that the air-velocity makes the same direction with the vertical as in the experiment in which the instrument is to be employed.

The linear relation expressed by formula (1) has been tested experimentally for velocities as low as 17 cm./sec.[†], and was found to hold good within limits of experimental error. Theoretically the linear relation mentioned is the asymptote to a transcendental curve expressing the true relation between heat-loss and velocity : it is shown, however, that to an accuracy of $2\frac{1}{2}$ per cent. a linear formula of the type (1) may theoretically be employed when the velocity is as low as that given by the relation $Vd = 1 \cdot 87 \times 10^{-2}$, V being expressed in cm./sec., and the diameter d in cm.[‡] For a $2\frac{1}{2}$-mil wire this limiting velocity is as low as $V = 2 \cdot 9$ cm./sec., probably much lower than the lower limit imposed by the disturbing effect of the free convection current.

* Reference (1), Table VIII., p. 424.
† Reference (1), Table III., p. 416.
‡ Reference (1), Description of Diagram I., p. 426.

Fig. 3.
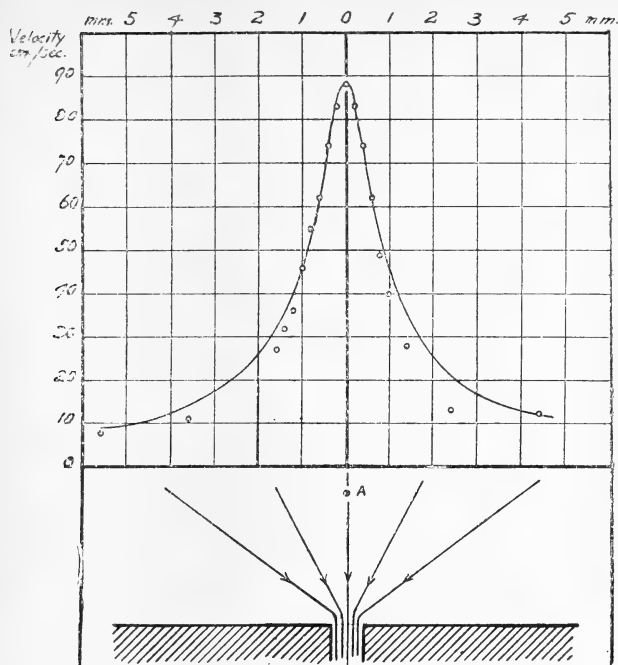
Test of Anemometer Readings at Low Velocities: *3-mil Wire No.* 7.

A short rectangular channel of width 0·75 mm., having a plate at right angles to its length fitted flush with its upper extremity, was set up in the manner illustrated in the lower part of the figure. By means of suitable connexions to a gasometer, air from the room was drawn into this channel under a constant pressure-difference of 2·35 cm. water. The distribution of flow at a sufficient distance from the opening of the channel is approximately that which would be set up in a perfect fluid by a distribution of sinks along a line coinciding with the opening of the channel into the plane mentioned. In the neighbourhood of a plane bisecting this slit at right angles, where the velocity is measured by the portion of the anemometer-wire between potential terminals, the distribution of velocity is approximately radial. Taking a set of axes (x, y) having as their plane the diametral plane just mentioned, with origin at the centre of the slit, and measuring the axis of y along the direction of the channel, the velocity at any point (x, y) is approximately given by $V = V_0 \sqrt{y^2/(y^2 + x^2)}$, V_0 being the maximum velocity at $x=0$. The anemometer-wire, represented by A in the figure, was set by means of a micrometer-screw in various positions in the plane $y=3$ mm.; the observed velocity distribution thus obtained was compared with the theoretical by choosing V_0 to agree with the experimental value at $x=0$. The figure shows that the readings of velocity are fairly accurate for velocities as low as 12 cm./sec.; the deviations are possibly due to the limitations of the simple formula employed in calculating the theoretical velocity distribution.

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For the study of velocities lower than 17 cm./sec. the writer has found the whirling-table method unsatisfactory, as elaborate precautions have to be taken against the disturbing effect of draughts, perfect air-stillness being very difficult to secure in an ordinary laboratory, while the correction for "swirl" is not easily made and theoretically and practically is proportionally greater at small velocities than at large ones [*]. A more promising method of calibration is to employ a horizontal or vertical rail along which a carriage can be driven at a measured velocity and arranged automatically to move smoothly backwards and forwards with constant speed over its range ; the rail need only be moderately long (2 or 3 metres), as the anemometer has no appreciable lag and little more than a second is required to obtain a balance on the galvanometer [†].

At high velocities the linear relation (1) was tested for velocities as high as $V = 900$ cm./sec., the usual upper limit at which anemometer-wires are calibrated by the writer in practice. From experiments on the flow of air between parallel planes, it appears that the calibration formula may be extended to velocities as high as 2800 cm./sec., making use of a 3-mil wire. An example of a test on this point is discussed under fig. 4 : the distribution of velocity of a stream of air issuing from a channel 0·75 mm. in width was measured at intervals of 0·05 mm. When the resulting curve, which attained a maximum of about 2800 cm./sec., was integrated to obtain the total flow in cm.^{3} per sec., a fair agreement was obtained with the value of the total flow measured from the rate of fall of the gasometer, the pressure-difference over the length of the channel remaining the same in the two cases. Above this velocity it was found difficult to work with wires of the usual length of about 5 cm., as transverse vibrations are liable to be set up which invalidate the readings and tend to break off the potential leads, while the tension on the wire required to destroy synchronization with the free period of a stretched wire in an air-current is near the breaking-point of the wire. The upper limit of velocity measurement might be increased almost indefinitely by shortening the wire or by using stouter wire; this step results, however, in diminished

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[*] Reference (1), Description of Diagram II., p. 428.

[†] For horizontal calibration a photometer-bench and carriage could well be used, while for vertical work the anemometer may be mounted, suitably counterpoised as one of the weights of an ordinary Atwood's Machine, the moving system being electrically driven. An excellent design for the purpose is the moving lamp photometer described by Trowbridge and Truesdell (Phys. Rev. iv. p. 290, Oct. 1914).

Fig. 4.
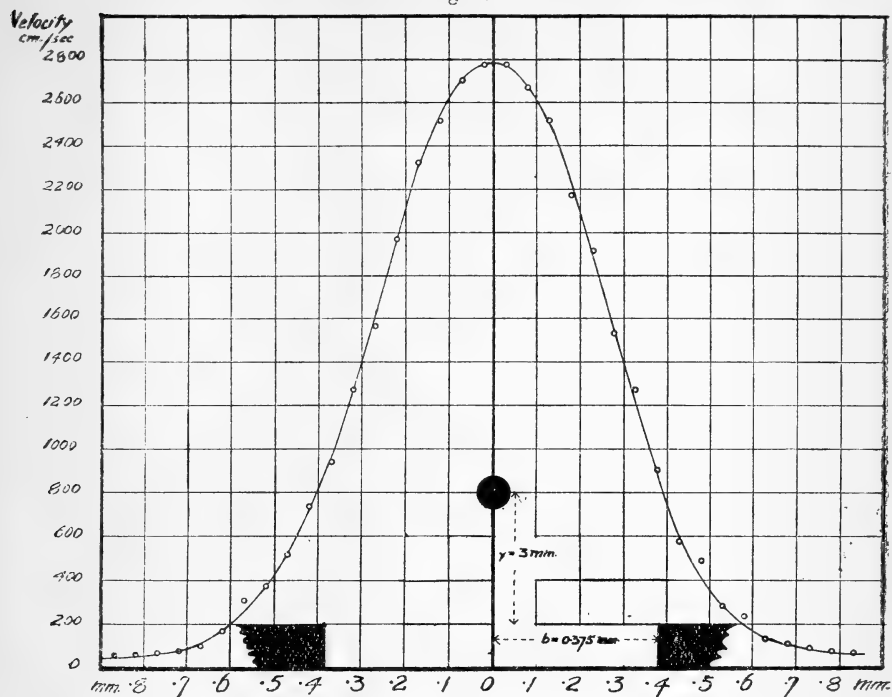
Test of Anemometer Readings at High Velocities: *3-mil Wire No. 7.*

The distribution of velocity illustrated in fig. 4 was measured by setting the anemometer-wire in various positions by means of a micrometer-screw in a plane at a distance $y=3$ mm. from the upper extremity of the channel described under fig. 3. The dimensions of the channel were:—width, $2b = 0.75$ mm.; breadth, $d = 5.08$ cm.; length, $l=5.06$ cm. Integrating this velocity-distribution between the limits $x = \pm 0.92$ mm., the total flow per unit breadth of channel is 182 cm.³/sec. under a pressure-difference of 11·5 cm. water. From a series of observations on the rate of fall of the gasometer for various pressure-differences, the total flow for breadth d was obtained, and hence the flow per unit breadth, assuming approximately uniform distribution of conditions over the breadth. From the curve connecting this flow with the pressure, the value per unit breadth corresponding to a pressure-difference of 11·5 cm. water came out to be 196 cm.³/sec., in fair agreement with the value obtained from the anemometer measurements; the latter is probably an underestimate, owing to the destruction of momentum of flow as the jet travels through the stagnant air in this region. The low velocities beyond the edges of the channel are due partly to a "diffusion" of the jet owing to its dragging action on the quiescent air through which it is flowing, and at a greater distance to an indraught of air from the surroundings into the moving air of the jet. The distribution of velocity over the channel approximates fairly well to a parabola.

sensitivity and resolving power, while in the use of stouter wire the working currents increase rapidly and the apparatus has to be specially designed to meet the resulting heating effects.

Section 3. On the Resolving Power of the Hot-Wire Anemometer.

By differentiating formula (3), we obtain

$$V/\delta V = \tfrac{1}{4}(i/\delta i)(1 - i_0{}^2/i^2). \quad . \quad . \quad . \quad (4)$$

We can conveniently define the "resolving power" of the anemometer by the ratio $V/\delta V$, where δV is the increment of velocity just observable at the velocity V. Formula (4) then expresses the resolving power of the anemometer in terms of that of the ammeter for current. In the ammeter employed by the writer the scale was uniformly graduated, and could be read to $\delta i = 0\cdot002$ ampere; on this basis the resolving powers of typical $2\tfrac{1}{2}$- and 3-mil wires are calculated for convenience of reference in Table I.

Table I.

Resolving Powers of $2\tfrac{1}{2}$- and 3-mil Anemometer-Wires.

$2\tfrac{1}{2}$-mil wire No. 17. $V=(i^2-0\cdot564)^2\times276\cdot4$ $\delta i=0\cdot002$ amp. $V/\delta V=\tfrac{1}{4}i/\delta i(1-0\cdot564/i^2)$.				3-mil wire No. 8. $V=(i^2-0\cdot81)^2\times116\cdot6$. $\delta i=0\cdot002$ amp. $V/\delta V=\tfrac{1}{4}i/\delta i(1-0\cdot81/i^2)$.			
$i.$	$V.$	$V/\delta V.$	$\delta V.$	$i.$	$V.$	$V/\delta V.$	$\delta V.$
amperes.	cm./sec.		cm./sec.	amperes.	cm./sec.		cm./sec.
0·90	16·7	34·2	0·48	1·10	18	45·4	0·40
1·00	52·4	54·5	0·96	1·20	46	65·5	0·70
1·50	785	141	5·6	1·80	684	170	4·00
2·00	3260	215	15·1	2·45	3150	264	12·0

In most applications the steadiness of velocity conditions is not sufficiently great to warrant making use of the full resolving power of the instrument; in experiments carried out by the writer on the flow of air between parallel planes an extremely good pressure regulation was maintained by means of the Töpler tilting manometer shown in Plate X.*, and it was found possible to make use of the full resolving power of the instrument. The observed resolving power at

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* For a description of this instrument, see a paper by A. Töpler, *Ann. d. Phys.* lvi. p. 610, 1895; also Müller-Pouillet, *Lehrbuch der Physik*, 1906, vol. i. p. 462.

various velocities was found to agree fairly well with the calculated values. If conditions are sufficiently steady, and a higher resolving power than this is required, the use of a Weston Laboratory Standard ammeter for which $\delta i = 0.0005$ ampere will give a fourfold increase in resolving power.

It is shown theoretically [*] that the disturbing effect of a thin wire in a uniform stream of fluid is extremely small ; at a distance of ten radii from the centre of the wire the velocity is only disturbed by 1 per cent. of its value, so that the velocity is practically measured at a point.

The anemometer employed by the writer was mounted on a micrometer-screw in the manner indicated in the photographic reproduction given in Plate X. Each division of the divided head corresponded to 1/100 mm., and it was found that in very steep gradients of velocity a movement of the wire of this magnitude resulted in an easily detectable change of velocity. The limit of the resolving power in a steep gradient is easily estimated by referring to fig. 4 ; a movement of the wire over a distance of 0.05 mm. resulted in an increase of velocity from 1570 to 1970 cm./sec. As the resolving power $V/\delta V$ of the wire employed is about 160, the change of velocity just detectable at the lower velocity is about 10 cm./sec. ; so that it is easily seen that a change of velocity of this amount can be detected in a distance of 1/800 mm. It is thus possible, by the use of the linear hot-wire anemometer, to measure velocity gradients as high as 80,000 cm./sec. per cm. In extremely sharp gradients, in which the velocity changes very greatly over a distance comparable to the diameter of the wire, a correction for the disturbance of flow and the effect of the gradient on the heat-loss might be appreciable. The correction is difficult to determine theoretically, but may, if necessary, be determined experimentally by measuring the same gradient by means of anemometer-wires of different radii. The fact that the total flow determined by integrating the velocity distribution of fig. 4 agrees with that determined directly, indicates that in gradients as high as 8×10^4 cm. sec. per cm. the corrections mentioned are probably small.

Section 4. SOURCES OF ERROR IN HOT-WIRE ANEMOMETRY.

(i.) *Disturbing Effect of the Anemometer-Fork and Wire.*

The special design of fork required to hold in position the anemometer-wire will depend largely on the nature of the work to be undertaken. By employing fine steel needles to

[*] Reference (1), p. 405.

hold in position the wire and potential terminals, the disturbing effect at the point of measurement is reduced to a minimum : moreover, the velocity actually measured is that over the interval between the potential terminals whose disturbing effect is practically nil, so that a " guard-ring " effect is obtained. The disturbing effect of the anemometer-wire itself has already been discussed in the preceding section, and is seen to be extremely small. As the wire is calibrated in a uniform stream in which the velocity is constant over the interval between potential terminals, care must be taken in using the instrument that the flow is also uniform over the measuring wire ; this condition is easily judged if the wire be employed at a high temperature so that it glows dull red, as in this case small variations of velocity can be detected with great accuracy by the unequal brightness of the wire. If the changes of velocity are too rapid to allow of an approximately uniform flow over the wire being brought about, the distance between potential terminals should be shortened until this condition is realized. In precision work care should also be taken that the conduction losses in the wire are the same under conditions of calibration as in actual use. This condition may be secured by so disposing the potential terminals that they occupy the same position relatively to the direction of flow under conditions of calibration as in the distribution of flow which it is required to investigate.

(ii.) *Effect of Variations of Atmospheric Conditions.*

It has been shown experimentally by the writer [*] that the heat-loss per unit length from a wire in a current of air of velocity V is given by a formula of the form

$$H = ri^2 = E + (\gamma + \beta \sqrt{V})(\theta - \theta_0), \quad . \quad . \quad (5)$$

r being the resistance of the wire per unit length when heated by a current i to a temperature $\theta - \theta_0$ above that of the atmosphere θ_0. E represents the radiation-loss in watts per unit length, calculated according to the formula [†]

$$E = 2\pi r \times 0.514 (\Theta/1000)^{5.2}, \quad . \quad . \quad . \quad (6)$$

Θ being the absolute temperature. An inspection of the tabulated heat-losses in the experiments previously referred

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[*] Reference (1), pp. 399–401.

[†] The constants of this formula are derived from the results of Lummer and Kurlbaum for polished platinum (*Verh. Deut. Phys. Ges.,* Berlin, xvii. p. 106, 1898).

to[*] will show that even at very low velocities and high temperatures the radiation-loss is only a small fraction of the total loss, and may therefore be neglected in studying the effect of small variations of atmospheric conditions on the heat-loss. The constants γ and β have small temperature coefficients given by

$$\gamma = \gamma_0[1 + 0\cdot00114(\theta - \theta_0)] \quad \text{and} \quad \beta = \beta_0[1 + 0\cdot00008(\theta - \theta_0)], \qquad \ldots \quad (7)$$

which may also be neglected in discussing the problem in hand.

According to the theoretical formula developed by the writer, and shown to be in substantial agreement with the results of experiments on the heat-loss from a cylindrical wire of radius a, we have

$$\gamma_0 = \kappa_0 \quad \text{and} \quad \beta_0 = 2\sqrt{\pi s_0 \sigma_0 \kappa_0 a_0}, \quad \ldots \quad (8)$$

κ_0 being the thermal conductivity of air, s_0 its specific heat per unit mass (at constant volume), and σ_0 its density ; the suffix $_0$ refers to the values of these constants under atmospheric conditions and at temperature θ_0.

Comparing the approximate theoretical formula

$$\mathrm{H} = ri^2 = (\gamma_0 + \beta_0 \sqrt{\mathrm{V}})(\theta - \theta_0) \quad \ldots \quad (9)$$

with the calibration formula

$$i^2 = i_0^2 + k\sqrt{\mathrm{V}}, \quad \ldots \ldots \quad (10)$$

we have

$$ri_0^2 = \gamma_0(\theta - \theta_0) \quad \text{and} \quad rk = \beta_0(\theta - \theta_0). \quad \ldots \quad (11)$$

An anemometer-wire is calibrated under given atmospheric conditions which do not affect the manganin resistance, and therefore also leave unaffected the resistance r and the temperature θ to which the wire is raised : it is required to determine the small correction $\delta \mathrm{V}$ which must be added to the velocity V corresponding to the observed current i when the atmospheric conditions are slightly altered. These are separately discussed under the headings of pressure, humidity, and temperature.

(α) *Effect of Variations of Atmospheric Pressure.*—
The study of the variation of the convection constants with pressure has recently been undertaken by Kennelly

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[*] Reference (1), Tables III. & IV., pp. 416 & 418.

and Sanborn [*]. The experiments were carried out over a range of pressures from $\frac{1}{2}$ to 3 atmospheres, and show that that part of the heat-loss depending on the velocity V varies as $\sqrt{\sigma_0}V$ over this range of pressures. This result is in agreement with what we should expect from the theoretical equation (9); and as it is well known that the thermal conductivity of a gas is independent of the pressure, it follows that the only factor in this equation which depends on the density is β_0. We thus have by differentiating (9) with respect to σ_0, the current i being given, the relation

$$\delta\beta_0/\beta_0 + \tfrac{1}{2}\delta V/V = 0.$$

From (8) $\delta\beta_0/\beta_0 = \tfrac{1}{2}\delta\sigma_0/\sigma_0 = \delta p_0/p_0$, where p_0 refers to atmospheric pressure, we obtain finally

$$\delta V \; V = -\delta p_0/p_0. \quad . \quad . \quad . \quad . \quad (12)$$

It will thus be seen that ordinary variations of pressure have a very small effect on velocity determinations; if they should be sufficiently large to affect appreciably the measurement of velocity, the corresponding correction may be made by the application of formula (12).

A compensating arrangement to correct for pressure changes might, if necessary, be devised: an inspection of formula (9), together with the experiments of Kennelly and Sanborn, show that the anemometer measures the product of the density and the velocity, that is, the mass-flow of a gas. From many practical points of view the measurement of mass-flow is the desideratum, and compensation is in these cases unnecessary.

(β) *Effect of Variations of Atmospheric Humidity.*—The extent to which the presence of water-vapour affects the various factors involving thermal conductivity and specific heat which enter into the theoretical formula (9) is difficult to foresee. As the proportion of water-vapour molecules even at saturation is relatively small, their influence

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[*] A. E. Kennelly and H. S. Sanborn, " The Influence of Atmospheric Pressure upon the Forced Thermal Convection from Small Electrically-Heated Platinum Wires," Proc. American Phil. Soc. vol. viii. 1914. The results of experiment are examined in the light of Boussinesq's formula,

$$H = 8\sqrt{(s\sigma\kappa V a/\pi)}(\Theta - \Theta_0).$$

It would be interesting to examine these results in the light of the emendation of Boussinesq's formula; small discrepancies at high and low pressures might thus be explained. The results given in the paper mentioned are not published completely enough to enable this to be done; moreover, an absolute comparison would not be satisfactory, as the velocities are considerably affected by " swirl," which would be difficult to allow for without a special determination.

may be judged to be small on the heat loss from the heated anemometer-wire. In fact this point was specially tested in the experiments of Kennelly and Sanborn referred * to with the result that no appreciable effect on the heat-loss due to this cause could be detected, although a small effect was thought possible. No disturbing effect on velocity determinations due to this cause has been noticed by the writer : it is hoped, however, to definitely settle this point by a special series of experiments.

(γ) *Effect of Variations of Atmospheric Temperature.*— Differentiating equation (2) with respect to θ_0, the current i being given, we easily obtain by making use of (10) and (11)

$$\delta V/V = 2\delta\theta_0/(\theta-\theta_0) . (1-i_0^2/i^2)^{-1}. \quad . \quad . \quad (13)$$

In the case of a $2\frac{1}{2}$-mil wire employed at 1000° C., $i_0^2 = 0.5$ approximately, while for a range of velocity from 50 to 2800 cm./sec. i varies between 1 and 2 amperes, so that the factor $(1-i_0^2/i^2)^{-1}$ varies from 2·00 to 1·14. It will be seen that by employing a wire in the neighbourhood of 1000° C. variations of room temperature of ± 2° C. give rise to errors of velocity determinations which at most are less than one per cent. If fluctuations of room temperature exceed this amount, the corresponding correction can easily be made by use of formula (13).

In the experiments carried out by the writer, the room temperature rarely fluctuated more than by ± 2° C., and as the wire was employed at a high temperature, it was not thought necessary to adopt temperature-compensating devices. The Kelvin Bridge connexions lend themselves extremely well to a compensating arrangement, which we proceed to describe. The fundamental relation $A/B = a/b = \alpha/\beta$ will remain valid at all temperatures if the resistances (B, b, β) are constructed of manganin, while (A, a, α) are of platinum or of a wire or combination of wires having the same equivalent temperature coefficient ϵ as the platinum anemometer-wire A. The coils (a, α) are so disposed that they can readily attain the temperature of the air-stream whose velocity it is required to measure. Under these circumstances if (a_0, α_0) refer to 0° C., while for convenience temperatures are measured on the platinum scale, we have

$$A = A_0(1+\epsilon\theta_p) \quad \text{and} \quad \alpha = \alpha_0(1+\epsilon\theta_{0p}). \quad . \quad (14)$$

When a balance is obtained on the bridge we have $A = B\alpha/\beta$,

* *Loc. cit.* p. 69.

so that the temperature θ_p attained by the anemometer-wire A is given by

$$A_0(1 + \epsilon\theta_p) = (B/\beta) \cdot \alpha_0(1 + \epsilon\theta_{0p}),$$

or more conveniently by

$$\theta_p - \theta_{0p} = (B/\beta) \cdot [\alpha_0/A_0 - \beta/B](1 + \epsilon\theta_{0p}). \quad . \quad (15)$$

To the order of approximation employed in (9) the law expressed by this formula will not be greatly altered if the temperatures are measured on the platinum scale, the effect being to alter the convection constants γ_0 and β_0 to slightly different values γ_0' and β_0' : hence if l denote the length of the anemometer-wire between potential terminals, we may write (9) in the form

$$Ai^2 = l(\gamma_0' + \beta_0'\sqrt{V})(\theta_p - \theta_{0p}),$$

which gives, on making use of (14) and (15),

$$(B/\beta)\alpha_0(1 + \epsilon\theta_{0p})i^2 = l(B/\beta) \cdot [\alpha_0/A_0 - \beta/B](\gamma_0' + \beta_0'\sqrt{V})(1 + \epsilon\theta_{0p}) ;$$

or finally,

$$\alpha_0 i^2 = l(\gamma_0' + \beta_0'\sqrt{V})[\alpha_0/A_0 - \beta/B]. \quad . \quad . \quad (16)$$

This formula indicates that to the first order of small corrections the determinations of velocity will be independent of room temperature.

In the practical realization of this system of compensation the ratio-coils (a, α) may be made of platinum or of some metal having the same temperature coefficient as platinum, but more conveniently by combining two resistances, either in series or in parallel, so that the equivalent resistance is of the required value and the equivalent temperature coefficient that of the anemometer-wire. It is easily proved that by employing wires whose temperature coefficients are respectively less and greater than that of platinum, the required combination can always be obtained and predetermined. The parallel combination is to be preferred, as its greater current-carrying capacity would materially lessen the danger of heating from this source. This point should be carefully tested for before these coils are inserted in the Kelvin Bridge. The current in the coils (α, β) and (a, b) are easily calculated in terms of the current through the anemometer-wire *, and these coils should be so wound as to dissipate heat as readily as possible in order that the change of resistance due to current-heating be entirely neglible for the

* Reference (1), p. 385.

maximum current employed in the velocity determinations. If the coils be wound bare in the form of an open grid, the current-heating may easily be predetermined from the data obtained from the writer's analysis of Langmuir's observations on the free convection of heat from small wires [*].

It may be noticed that temperature-compensation may also be obtained by constructing (a, b, α, β) of manganin, and B of a wire, or combination of wires, having the same temperature coefficient as the anemometer-wire and of sufficient current-carrying capacity to be unaffected by the heating effect of the measuring current. It is easily seen that this arrangement is not as satisfactory as that already discussed, since this resistance must be easily capable of adjustment as different anemometer-wires are inserted in the circuit.

(iii.) *Ageing and Life of Anemometer-Wires.*

The comparative immunity of the hot-wire anemometer from serious corrections due to such fluctuations of room-temperature as may ordinarily occur in a laboratory, is secured by the use of a wire at a high temperature, this being rendered possible for accurate work by the employment of the Kelvin Bridge connexions. The limitation in the direction of high temperatures is a slow progressive increase in the resistance of the wire due to "evaporation"; the effect which will be referred to as "ageing" increases for very thin wires, and in practice sets a lower limit to the diameter of the wire which it is possible to employ for any considerable length of time at about $2\frac{1}{2}$ mils. Experience has shown that in the case of a wire of this diameter the ageing becomes distinctly noticeable after the wire has been employed to measure about 1000 velocities. In Table II. are given two calibration formulæ for the same wire separated by 1060 velocity determinations, showing that at the high temperature of 1000° C. employed the ageing becomes distinct only after extended use. For this reason it is desirable to employ the wire at as low a temperature as is consistent with the source of error represented by (13) being considered sufficiently small for the purpose in hand; also if durability is required to use a larger wire. In precision measurements of velocity it is advisable to recalibrate the wire at intervals of about 500 observations; the necessary whirling arm is easily improvised with materials which are available in a laboratory [†], and the necessary calibration only

[*] Reference (1), Description of Table VIII., p. 424.
[†] Reference (1) p. 428, Diagram II.; also Plate 8 (a).

occupies about an hour's time. The necessary corrections for ageing are easily applied by dividing the observations into groups of 100 and applying proportional velocity-corrections to each group. In the case of wire No. 17, given in Table II., it was found that the correction for "ageing" corresponding to 100 readings was a little less than the change of velocity just detectable by the instrument.

The life of the anemometer-wires depends to a large extent on conditions of service. In the measurement of steep gradients of velocity the risk of burning out is considerable, and during the course of the writer's experiments was the cause of failure of most of the wires. It is seen from Table II. that the life usually ranges from 500 to 1000 velocity observations.

Table II.

Wire No.	Diameter.	Maximum velocity.	Life in number of velocity determinations.	Calibration formulæ for Wire 17.
7	3 mil	2930 cm./sec.	500	(1) $V=(i^2-0.564)^2\times276.4$
8	3	2500	540	(2) $V=(i^2-0.545)^2\times286.3$ (3) $V=(i^2-0.535)^3\times236.3$
14	2.5	1100	900	Formulæ (1) and (2) were separated by 1060 observations and show the
16	2.5	1000	700	effect of ageing. Formula (3) was derived from ob-
17	2.5	1150	1700	servations immediately following (2), and shows the agreement obtained by calculating the constants from the line of closest fit.

For purposes of continuous recording it is necessary to employ a wire at a somewhat lower temperature : the resulting error due to changes of atmospheric temperature can be eliminated by the use of the compensating ratio-coils already discussed. In this way the life of the wires should be considerably lengthened and the ageing diminished ; the margin of galvanometer-sensitivity is ample to meet the resulting diminution of sensitiveness. The writer has found in many cases that the use of a wire at a dull red temperature in allowing conditions of flow to be readily judged by inspection, is an advantage which compensates in large measure the disadvantage of being obliged to recalibrate the wire at intervals to determine the correction due to ageing.

Section 5. Notes on Various Applications of the Hot-Wire Anemometer.

The high resolving power, comparative freedom from serious corrections, together with extreme sensitiveness at low velocities, make the linear anemometer a very suitable laboratory instrument for use in studying various problems of gas-flow. In particular the instrument has recently been employed by the writer in a detailed investigation on the flow of air between parallel planes, with especial reference to the study of criteria of stability of laminar flow ; in fact, the system of precision anemometry described in the present paper was evolved with special reference to this problem. The detailed analysis of velocity gradients furnishes a new method of attacking problems of gaseous viscosity, while investigations on the heat-loss from a wire at different velocities, pressures and temperatures promise to throw much light on phenomena relating thermal conduction in cases.

In the course of the investigation referred to, and which it is hoped to publish shortly, it was found necessary to take many thousand observations ; although it was found possible to make as many as 100 velocity determinations an hour, and to reduce them very rapidly in the manner already indicated, it is easily seen that more extended investigations of this type will require very considerable routine labour. The equipment necessary for work of this kind is not usually available in a physical laboratory, and the prosecution of research of this type is better suited to the resources and personnel of modern aerotechnical laboratories. In this field the linear anemometer described would seem to have a wide field of usefulness as a standard instrument, the need for which is several times emphasized in the 1912–13 Technical Report of the Advisory Committee for Aeronautics [*]. There is no doubt that a compilation of results obtained in this way would assist very materially in the development of a rational theory relating to many problems of aerodynamic resistance. A recording form of instrument is now under investigation by the writer, and it is hoped by this means to very materially lessen the labour of taking observations ; it is also hoped to do away with the necessity of calibrating anemometer-wires by arranging that previously calibrated wires be issued from a reliable firm of instrument-makers : the Kelvin Bridge connexions makes the insertion of such calibrated wires, with potential terminals already fused in place, possible without risk of introducing error due to imperfect contacts.

[*] Darling & Son, London, 1914, President's Report, p. 16.

The non-compensated Kelvin Bridge and anemometer can easily be employed to analyse gas-temperatures as well as velocities. The special feature of these connexions already mentioned eliminates the error due to variation of temperature along the length of the current- and potential-connecting wires and the same advantage is obtained as in Callendar's system of compensated leads in platinum thermometry. When using the anemometer-wire as a linear thermometer, it is necessary to employ a very small measuring-current and a more sensitive galvanometer than in velocity measurements; the resistance B is reduced to the proper value by shunting by means of a suitable manganin resistance, and fine adjustments are made by including in parallel an adjustable high resistance such as that which forms the essential part of the Kelvin Varley potentiometer. If temperature distribution is to be measured in a stream of air at high velocities correction should be made for the "kinetic heating," *i.e.*, the heating-effect due to the impact of the air-molecules on the wire. From some experiments of the writer, this kinetic heating-effect is roughly proportional to the square of the velocity, and is about 1° C. at 1500 cm./sec. in the case of a $2\frac{1}{2}$ mil-wire[*]. If very accurate temperatures are required the measuring-current should be varied and temperatures extrapolated to zero current. By proceeding in this manner the writer has succeeded in measuring temperature as well as velocity distributions to 1/100 of a degree C., making use of a galvanometer of sensitivity 10^{-9} ampere. This additional property renders the hot-wire anemometer useful in investigating conditions of heat-transfer from gases and liquids to solid surfaces; data on these points would be of importance in many technical problems relating to methods of air-cooling of internal-combustion engines, oil-cooling of electrical transformers, and the ventilation of electrical machinery.

In connexion with the modern types of oscillograph the employment of the anemometer in the measurement of variable gas velocities and temperatures might furnish results of value in many engineering problems.

In technical problems relating to the measurement and recording of gas-flow in pipes, the anemometer employed in the form considered would seem capable of useful developments; its property of measuring the mass-flow at all pressures has already been mentioned. In particular, the application to the measurement of steam-flow would give

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[*] Compare the experiments of Joule and Thomson, Trans. Roy. Soc. June, 1860; Kelvin, 'Collected Works,' vol. i. pp. 900-914.

recorded data from which might be obtained the efficiency of any steam-operated engine. In the case of the steam turbine, the possibility of obtaining a record of performance analogous to the indicator-diagram of the ordinary recipro-cating engine might make the subject worthy of a special investigation.

In closing, the writer has much pleasure in thanking Professor H. T. Barnes, F.R.S., Director of the Macdonald Physics Laboratory, for the kind way he has facilitated the present work by every means in his power.

Summary.

(1) Specifications relating to the construction of the linear hot-wire anemometer are given in detail ; by means of the Kelvin Double Bridge connexions it is possible to employ wires at high temperatures, thus making velocity determinations practically independent of ordinary fluctua-tions of room temperatures.

(2) The most suitable methods of determining the con-stants of the calibration formula $i^2 = i_0{}^2 + k\sqrt{V}$ are discussed, together with evidence as to accuracy of registration for velocities less than 50 cm./sec. and greater than 900 cm./sec., these being the limits usually employed in calibrating anemometer-wires.

(3) If the change of velocity just detectable by the in-strument is denoted by δV, the ratio $V/\delta V$ which defines the resolving power of the anemometer is expressed in terms of that of the ammeter employed in connexion with the apparatus ; it is shown that with an ammeter reading to 0·002 ampere the resolving power of a $2\frac{1}{2}$-mil wire at $V = 800$cm./sec. is about 140, and the change of velocity just detectable is about 6 cm./sec..

(4) Various sources of error are considered in detail ; effects of variations of atmospheric pressure, humidity, and temperature are dealt with and are shown to be negligible under ordinary circumstances if a high-temperature wire be employed. Data are given on the ageing and life of anemo-meter-wires. It is shown that the anemometer measures the mass-flow of a gas ; a compensating arrangement of ratio-coils is described which eliminates variations of room temperature as a source of error.

(5) Applications of the hot-wire anemometer to physical and technical problems are described.

McGill University,
Nov. 19th, 1914.

LVIII. *On the Coefficients of Self and Mutual Induction of Coaxial Coils.* By S. BUTTERWORTH, *M.Sc., Lecturer in Physics, School of Technology, Manchester**.

1. ALTHOUGH many formulæ have been given for the mutual induction of coaxial circles and solenoids, little seems to have been done on the mutual induction of coils for which the ratio of the inner and outer diameters differs considerably from unity. The present investigation is to supply suitable formulæ for such cases.

The method adopted is to find the mutual induction between two mutually external semi-infinite coaxial coils having zero core diameters and unit winding density (*i.e.* the number of turns per unit area of channel section is unity), and then by applying the laws of combination of mutual inductances to find the mutual induction between finite hollow coils.

The results are extended so as to include self-induction.

The semi-infinite coils of the nature indicated will, for brevity, be referred to as "solid coils." If we take the radius of the larger coil as the unit of length, then only two variables are involved, viz. : the radius of the smaller coil ranging from zero to unity and the distance of the coil faces. Dimensional considerations will give the correct formula when the radius of the larger coil is not unity.

2. For any magnetic field possessing circular symmetry about an axis, the magnetic potential Ω satisfies the equation

$$\frac{\partial^2\Omega}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial\Omega}{\partial\rho} + \frac{\partial^2\Omega}{\partial z^2} = 0, \quad \ldots \quad (1)$$

in which z represents the distance along, and ρ the distance from the axis of symmetry. A solution of this equation is

$$\Omega = \int_0^\infty \phi(\lambda)e^{-\lambda z} J_0(\lambda\rho)d\lambda \quad \ldots \quad (2)$$

reducing when $\rho=0$ to

$$\Omega_0 = \int_0^\infty \phi(\lambda)e^{-\lambda z} d\lambda. \quad \ldots \quad (3)$$

If Φ is the stream function (*i. e.* the magnetic flux through

a circle of radius ρ and centre at z, 0), then

$$\Phi = -2\pi \int_0^{\rho} \rho \frac{\partial \Omega}{\partial z} d\rho$$

$$= 2\pi\rho \int_0^{\infty} \phi(\lambda) e^{-\lambda z} J_1(\lambda\rho) d\lambda ; \quad . \quad . \quad . \quad (4)$$

or on expanding $J_1(\lambda\rho)$ in ascending powers of ρ and making use of (3),

$$\Phi = -\pi\rho^2 \sum_0^{\infty} (-)^n \left(\frac{\rho}{2}\right)^{2n} \frac{1}{\lfloor n \ \lfloor n+1} \frac{d^{2n+1}\Omega_0}{dz^{2n+1}} \quad . \quad . \quad (5)$$

so that Φ can be found at all points if the potential at all points along the axis of symmetry is given.

Now let a solid coil of radius r extending from z to infinity be placed with its axis along the axis of symmetry. The number of linkages that the field makes with this coil is

$$N = \int_0^r d\rho \int_z^{\infty} \Phi dz$$

$$= \pi r^3 \sum_0^{\infty} \frac{(-)^n}{2^{2n}} \frac{r^{2n}}{(2n+3) \lfloor n \ \lfloor n+1} \frac{d^{2n}\Omega_0}{dz^{2n}} \quad . \quad . \quad (6)$$

3. If Ω_0 is due to a second solid coil of unit radius extending from $z=0$ to $z=-\infty$, then

$$\Omega_0 = 2\pi \int_0^1 (\sqrt{\rho^2 + z^2} - \rho) d\rho$$

$$= \pi(z^2 \log \frac{1+\zeta}{z} + \zeta - 2z), \quad . \quad . \quad (7)$$

where $\zeta^2 = 1 + z^2$.

If z is large then (7) may be expanded in inverse powers of z giving

$$\frac{\Omega_0}{2\pi} = \frac{1}{2z} \sum_{s=0}^{s=\infty} \frac{(-)^s \lfloor 2s}{(2s+3) \lfloor s \ \lfloor s+1} \frac{1}{(2z)^{2s}}, \quad . \quad . \quad . \quad (8)$$

so that

$$\frac{1}{2\pi} \frac{d^{2n}\Omega_0}{dz^{2n}} = \frac{1}{2z^{2n+1}} \sum_{s=0}^{s=\infty} \frac{(-)^s \lfloor 2(n+s)}{(2s+3) \lfloor s \ \lfloor s+1} \frac{1}{(2z)^{2s}}. \quad . \quad (9)$$

2 P 2

Inserting (9) in (6) and rearranging so as to express N in inverse powers of z,

$$\frac{Nz}{\pi^2 r^3} = \sum_{p=0}^{p=\infty} \frac{(-)^p \lfloor 2p}{(2z)^{2p}} \sum_{n=0}^{n=p} \frac{r^{2n}}{(2n+3)(2p-2n+3)\lfloor n \lfloor p-n \rfloor n+1 \lfloor p-n+1}$$

. . . (10)

or on expansion

$$\frac{Nz}{\pi^2 r^3} = \frac{1}{9} - \frac{1}{(2z)^2}\left(\frac{1}{15} + \frac{r^2}{15}\right) + \frac{1}{(2z)^4}\left(\frac{2}{21} + \frac{6}{25}r^2 + \frac{2}{21}r^4\right)$$

$$- \frac{1}{(2z)^6}\left(\frac{5}{27} + \frac{6}{7}r^2 + \frac{6}{7}r^4 + \frac{5}{27}r^6\right)$$

$$+ \frac{1}{(2z)^8}\left(\frac{14}{33} + \frac{28}{9}r^2 + \frac{40}{7}r^4 + \frac{28}{9}r^6 + \frac{14}{33}r^8\right)$$

$$- \quad \ldots\ldots \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (A)$$

From this formula, N (which represents the mutual induction between the two solid coils) can be obtained to 1 in 100,000 if $z > 3$.

4. When z is small (7) may be expanded in direct powers of z giving

$$\frac{\Omega_0}{2\pi} = \frac{1}{2} - z + \frac{1}{2}z^2\left(\left(\log \frac{2}{z} + \frac{1}{2}\right)\right)$$

$$+ \sum_{s=2}^{s=\infty} \frac{(-)^s}{2^{2s-1}} \frac{\lfloor 2s-3}{\lfloor s \lfloor s-1} z^{2s}. \quad . \quad . \quad . \quad (11)$$

In this formula the factor $-\frac{1}{2}z^2 \log z$ requires special treatment. Denoting it by $\omega/2\pi$,

$$\frac{1}{2\pi}\frac{d^2\omega}{dz^2} = -\left(\log z + \frac{3}{2}\right), \quad \frac{1}{2\pi}\frac{d^{2n}\omega}{dz^{2n}} = \frac{2n-3}{z^{2n-2}}.$$

Hence by (6), if n represents the number of linkages due to ω,

$$\frac{\ddot{z}}{2\pi^2 r^3} = -\frac{1}{6}z^2 \log z + \frac{r^2}{40}\left(\log z + \frac{3}{2}\right)$$

$$+ z^2 \sum_{n=2}^{n=\infty} \frac{(-)^n}{(2n+3)} \frac{\lfloor 2n-3}{\lfloor n \lfloor n+1}\left(\frac{r}{2z}\right)^{2n} \quad . \quad . \quad . \quad (12)$$

This converges so long as $z > r$.

For the remaining portion of Ω_0 it is preferable to retain the finite form (7) because of the slow convergence of (11).

Hence as a working formula for $z > r$ we have

$$\frac{N}{2\pi^2 r^3} = A - (B - \alpha) r^2 + C r^4 - D r^6 \quad . \quad . \quad . \quad \text{(B)}$$

in which

$$3 A = \frac{1}{2} z^2 \log \frac{1 + \zeta}{z} + \frac{1}{2} \zeta - z \equiv \frac{\Omega_0}{2\pi} \left.\begin{array}{c}\\\\\\\\\\\\\end{array}\right\}$$

$$40 B = \log \frac{1 + \zeta}{z} - \frac{1}{\zeta} \equiv \frac{1}{2\pi} \frac{d^2 \Omega_0}{dz^2}$$

$$1344\, C = -\frac{1}{\zeta}\left(\frac{1}{1+\zeta} + \frac{1}{\zeta^2} - \frac{3}{\zeta^4}\right) \qquad \left.\begin{array}{c}\\\\\\\end{array}\right\} \quad . \quad . \quad . \quad \text{(B')}$$

$$82{,}944\, D = \frac{3}{\zeta}\left(\frac{1}{(1+\zeta)^2} - \frac{1}{\zeta^2} - \frac{3}{\zeta^4} + \frac{35}{\zeta^6} - \frac{35}{\zeta^8}\right)$$

$$\alpha = \left(\frac{z}{r}\right)^2 \sum_{n=2}^{n=\infty} \frac{(-)^n \lfloor 2n-3}{(2n+3)\,\lfloor n \,\lfloor n+1} \left(\frac{r}{2z}\right)^{2n}$$

If we use the series formulæ (8) and (9) for $3\,A$ and $40\,B$, when $z > 2$ the range of formula (B) is $4 > z > r$.

5. When z is less than r, the method followed in the preceding sections fails to give a convergent series, because of the logarithmic term in (11). For this case the method adopted is to find some simple magnetic distribution which will give rise to an axial potential containing the term $\pi z^2 \log z$ and other terms for which the preceding method is applicable. The linkages due to this distribution are calculated by direct integration, while those due to the terms not containing $\log z$ are found by the preceding method. The difference between the two results gives the linkages due to $\pi z^2 \log z$.

Let there be a linear distribution of poles on the axis of z extending from $z = 0$ to $z = -c$, and having a density πz^2. The potential at z due to this distribution is

$$\omega' = \pi \int_z^{c+z} \frac{(x-z)^2}{x} \, dx$$

$$= \omega + \pi \left\{ z^2 \log(c+z) - 2cz + \frac{c^2}{2} \right\}, \quad . \quad . \quad \text{(13)}$$

in which as before $\omega = -\pi z^2 \log z$.

Since we only require the linkages n corresponding to ω, we can choose c to have any convenient value. It will be supposed that c is very large. Then, by the method of

Section 2, if n' are the linkages corresponding to ω',

$$\frac{n'-n}{2\pi^2 r^3} = \frac{1}{3}\left\{\frac{1}{2}z^2\log(c+z)-cz+\frac{c^2}{4}\right\} - \frac{r^2}{40}\log(c+z)$$

$$+ \text{ terms which vanish when } c \text{ is infinite. } . \quad (14)$$

To obtain the linkages n' by direct integration we must find the work to be done to remove the linear magnetic distribution from the field due to the solid coil of radius r whose (south-seeking) pole is at z, 0.

Now the axial potential at a distance x from this pole is by (7)

$$-\Omega_0(x,\,r) = -\pi\left(x^2\log\frac{r+\sqrt{r^2+x^2}}{x} + r\sqrt{r^2+x^2}-2rx\right),(15)$$

and

$$n' = -\pi\int_z^{c+z}(x-z)^2\Omega_0(x,\,r)dx \quad . \quad . \quad . \quad (16)$$

By direct integration,

$$\frac{1}{\pi}\int^x (x-z)^2\Omega_0(x,r)dx$$

$$= \left(\frac{1}{5}x^5-\frac{1}{2}x^4z+\frac{1}{3}x^3z^2\right)\log\frac{r+\sqrt{r^2+x^2}}{x}$$

$$-\left(\frac{1}{20}r^5-\frac{1}{3}r^3z^2\right)\log\frac{x+\sqrt{r^2+x^2}}{r}$$

$$+r\sqrt{r^2+x^2}\left(\frac{3}{10}x^3+\frac{1}{20}xr^2-\frac{5}{6}x^2z-\frac{1}{3}r^2z+\frac{2}{3}xz^2\right)$$

$$-2r\left(x^4-\frac{2}{3}x^3z+\frac{1}{2}x^2z^2\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

$$= -\frac{1}{3}r^4z \text{ (when } x=0\text{).}$$

Putting $x=c+z$, and supposing c large, (17) becomes

$$\frac{r^3}{6}\left\{2z^2\log\frac{2(c+z)}{r}-\frac{4}{3}z^2-2cz+c^2\right\}$$

$$-\frac{r^5}{20}\left\{\log\frac{2(c+z)}{r}-\frac{1}{20}\right\}$$

$$+ \text{ terms which vanish when } c \text{ is infinite. } . \quad (18)$$

When x is small, the integration (17) can be obtained in series by using the form (11) for Ω_0, and integrating term by term, the constant of integration being $-\frac{1}{3}r^4z$ to correspond with (18).

Using this method for the lower limit of (16), and combining with (14),

$$\frac{n}{2\pi^2 r^3} = \frac{1}{3}\left(\frac{1}{2}z^2\log\frac{2}{r} - \frac{1}{3}z^2\right) - \frac{r^2}{40}\left(\log\frac{2}{r} - \frac{1}{20}\right)$$

$$+ \frac{r^2}{2}\left\{\frac{1}{3}\frac{z}{r} - \frac{1}{3}\frac{z^3}{r^3} + \frac{1}{6}\frac{z^4}{r^4} - \frac{1}{30}\frac{z^5}{r^5}\left(\log\frac{2r}{z} + \frac{77}{60}\right)\right.$$

$$\left. - \frac{z^3}{r^3}\sum_{n=2}^{n=\infty}\frac{(-)^n}{2^{2n-2}}\frac{\underline{|2n-3}}{\underline{|n-1}\,\underline{|n+1}}\frac{z^{2n}/r^{2n}}{(2n+1)(2n+3)}\right\}. \quad (19)$$

Using this to replace (12), we have instead of (B),

$$\frac{N}{2\pi^2 r^3} = \left(\frac{z^2}{6} - \frac{r^2}{40}\right)\log\frac{1}{r} + A' - (B'-\beta)r^2 + Cr^4 - Dr^6. \quad (C)$$

in which

$$3A' = \frac{1}{2}z^2\log 2(1+\zeta) + \frac{1}{2}\zeta - z - \frac{1}{3}z^2,$$

$$40B' = \log 2(1+\zeta) - \frac{1}{\zeta} + \frac{29}{20},$$

$$\beta = \frac{z}{2r}\left\{\frac{1}{3} - \frac{1}{3}\frac{z^2}{r^2} + \frac{1}{6}\frac{z^3}{r^3} - \frac{1}{30}\frac{z^4}{r^4}\left(\log\frac{2r}{z} + \frac{77}{60}\right)\right. \qquad \left.\vphantom{\sum}\right\} \quad (C')$$

$$\left. - \frac{z^2}{r^2}\sum_{n=2}^{n=\infty}\frac{(-)^n}{2^{2n-2}}\frac{\underline{|2n-3}}{\underline{|n-1}\,\underline{|n+1}}\frac{z^{2n}/r^{2n}}{(2n+1)(2n+3)}\right\}$$

6. When $z=0$, (19) becomes

$$\frac{n}{2\pi^2 r^3} = -\frac{r^2}{40}\left(\log\frac{2}{r} - \frac{1}{20}\right). \quad \cdots \quad (20)$$

Hence by (6) and (11),

$$\frac{N}{2\pi^2 r^3} = \frac{1}{6} - \frac{r^2}{40}\left(\log\frac{4}{r} + \frac{9}{20}\right) + \frac{1}{2}r^4\sigma, \quad \cdots \quad (D)$$

where

$$\sigma = \sum_{n=2}^{n=\infty}\frac{\underline{|2n-3}\,\underline{|2n}}{2^{4n-2}(2n+3)\,\underline{|n}\,\underline{|n}\,\underline{|n-1}\,\underline{|n+1}}\cdots r^{2n-4}$$

$$= \sum_{0}^{\infty}\left(\frac{1.3.5\ldots\ldots 2n+3}{2.4.6\ldots\ldots 2n+4}\right)^2\frac{r^{2n}}{(2n+7)(2n+3)(n+3)(n+1)}.$$

7. As a check on this result, the case of $z=0$ will now be treated by another method, involving elliptic integrals. The method is to start with the known elliptic integral formula for the mutual induction between two coaxial solenoids and,

by integration, to find the mutual induction between two solid coils.

Certain reduction formulæ are required, and these will be dealt with first. If E and K are complete elliptic integrals of the first and second kind to modulus x, then

$$\frac{dE}{dx} = \frac{E-K}{x}, \quad \frac{dK}{dx} = \frac{E}{x(1-x^2)} - \frac{K}{x}. \quad . \quad . \quad (21)$$

From (21) we readily derive the following reduction formulæ,

$$(n+2)\int x^n E dx = x^{n+1}E + \int x^n K dx \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

$$(n+2)^2 \int x^{n+2} K dx = x^{n+1}E - (n+2)x^{n+1}(1-x^2)K$$
$$+ (n+1)^2 \int x^n K dx \quad . \quad . \quad . \quad (23)$$

$$\int \frac{E}{x^2} dx = \left(\frac{1}{x} - x\right)K - 2\frac{E}{x}, \quad . \quad . \quad . \quad . \quad . \quad (24)$$

by means of which $\int x^n E dx$, $\int x^n K dx$ can be expressed in terms of E, K, $\int K dx$ and $\int \frac{K}{x}$, if n is any integer positive or negative.

In the succeeding work we are particularly concerned with

$$u = \int_0^x K\, dx, \quad \text{and} \quad v = \int_x^1 \frac{K}{x}\, dx. \quad . \quad . \quad (25)$$

Expressing K in series,

$$u = \frac{\pi}{2} x \left\{ 1 + \sum_1^\infty \left(\frac{1.3.5 \dots 2n-1}{2.4.6 \dots 2n}\right)^2 \frac{x^{2n}}{2n+1} \right\}. \quad (26)$$

When $x=1$,

$$u = u_1 = \int_0^{\frac{\pi}{2}} d\theta \int_0^1 \frac{dx}{(1-x^2\sin^2\theta)^{\frac{1}{2}}} = \int_0^{\frac{\pi}{2}} \frac{\theta d\theta}{\sin\theta}$$
$$= 2\left(1 - \frac{1}{3^2} + \frac{1}{5^2} - \dots\right) = 1 \cdot 83193. \quad . \quad . \quad (27)$$

Also

$$v = \int_0^{\frac{\pi}{2}} d\theta \int_x^1 \frac{dx}{x(1 - x^2 \sin^2 \theta)^{\frac{1}{2}}} = \int_0^{\frac{\pi}{2}} d\theta \int_{x \sin \theta}^{\sin \theta} \frac{dy}{y(1-y^2)^{\frac{1}{2}}}$$

$$= \frac{\pi}{2} \int_x^1 \frac{dy}{y(1-y^2)^{\frac{1}{2}}} - \int_0^{\frac{\pi}{2}} \frac{\theta d\theta}{\sin \theta} + \int_0^{\frac{\pi}{2}} \frac{\theta \cot \theta d\theta}{(1 - x^2 \sin^2 \theta)^{\frac{1}{2}}} \quad \cdot \quad \cdot \quad (28)$$

by integration by parts.

Performing the last integral of (28) by expanding $(1 - x^2 \sin^2 \theta)^{-\frac{1}{2}}$ in ascending powers of x, and integrating term by term,

$$v + u_1 = \frac{\pi}{2} \left\{ \log \frac{4}{x} - \sum_1^{\infty} \left(\frac{1 \cdot 3 \cdot 5 \, \ldots \ldots \, 2n-1}{2 \cdot 4 \cdot 6 \, \ldots \ldots \, 2n} \right)^2 \frac{x^{2n}}{2n} \right\}. \quad \cdot \quad (29)$$

8. The mutual induction between two semi-infinite co-axial cylinders of radii a and b, external to each other and with their ends in contact, is

$$m = \frac{8}{3} \pi a \{ (a^2 + b^2)\mathrm{E} - (a^2 - b^2)\mathrm{K} \}, \quad \cdot \quad \cdot \quad (30)$$

the linear winding density being unity, and the modulus of E and K being b/a, with $a > b$.

The mutual induction between a solenoid of radius a and a solid coil of radius b $(a > b)$ with their ends in contact is

$$m_1 = \frac{8}{3} \pi a \int_0^b \left\{ (a^2 + b^2)\mathrm{E} - (a^2 - b^2)\mathrm{K} \right\} db, \quad \cdot \quad (31)$$

which on applying the reduction formulæ becomes

$$m_1 = \frac{1}{3} \pi a^4 \left\{ \left(\frac{13}{2} + 2\frac{b^2}{a^2} \right) \frac{b}{a} \mathrm{E} - 5 \left(1 - \frac{b^2}{a^2} \right) \frac{b}{a} \mathrm{K} - \frac{3}{2} u \right\}. \quad \cdot \quad (32)$$

When $b = a$,

$$m_1 = m_2 = \frac{1}{3} \pi b^4 \left(\frac{17}{2} - \frac{3}{2} u_1 \right). \quad \cdot \quad \cdot \quad \cdot \quad (33)$$

The mutual induction between a solenoid of radius b and a solid coil of radius a $(a > b)$ with their ends in contact is

$$m_3 = m_2 + \int_b^a m \, da$$

$$= \frac{1}{3} \pi a^4 \left\{ \left(2 + \frac{13}{2} \frac{b^2}{a^2} \right) \mathrm{E} - \frac{1}{2} \left(4 - \frac{b^2}{a^2} - 3\frac{b^4}{a^4} \right) \mathrm{K} \right.$$

$$\left. - \frac{3}{2} \frac{b^4}{a^4} (v + u_1) \right\}. \quad \cdot \quad (34)$$

Finally, the mutual induction between two solid coils of radii a and b with their ends in contact is

$$N = \int_0^b m_3 \, db$$

$$= \frac{\pi a^5}{30} \{ 17r(1+r^2)E - r(14+3r^2)(1-r^2)K$$
$$- 3u - 3r^5(v+u_1) \}. \quad . \quad (35)$$

in which $r = b/a$.

When $r = 1$,

$$N = \frac{\pi a^5}{15}(17 - 3u_1) = 2\cdot4094 \, a^5 \text{ (by (27))}. \quad . \quad (36)$$

Inserting the series for E, K, u, v in (35) we find

$$\frac{N}{2\pi^2 a^5} = \frac{r^3}{6} \left\{ 1 - \frac{3}{20} r^2 \left(\log \frac{4}{r} + \frac{9}{20} \right) + 3r^4 \sigma \right\}, \quad (37)$$

where

$$\sigma = \sum_0^\infty \left(\frac{1 \cdot 3 \cdot 5 \dots 2n+3}{2 \cdot 4 \cdot 6 \dots 2n+4} \right)^2 \frac{r^{2n}}{(2n+7)(2n+3)(n+3)(n+1)}. \quad (38)$$

This result is identical with formula (D).

When $r = 1$, we find (to five figures)

$$N = 2\cdot4094 \, a^5,$$

which is in agreement with (36).

9. By means of formulæ (A), (B), (C), and (D) it is possible to evaluate N for all values of z, and all values of r up to unity.

The formulæ have the following ranges :—

$$\text{(A)} \quad z > 3, \qquad \text{(B)} \quad 4 > z > r,$$
$$\text{(C)} \quad r > z > 0, \qquad \text{(D)} \quad z = 0.$$

Table I. shows the agreement of (A) and (B) when $z = 4$; Table II. shows the agreement of (B) and (C) when $z = r$; $\frac{N}{2\pi^2 r^3}$ being the numbers tabulated.

In Table III. are tabulated $\xi = \frac{N}{2\pi^2 r^3}$, for $z < 4$, and in Table IV. are $\eta = \frac{1}{9} - \frac{Nz}{\pi^2 r^3}$, the forms ξ and η being chosen as being the most suitable for graphical interpolation. For interpolation in η it is convenient to notice that η is almost linear in r^2 and in $1/z^2$.

TABLE I. $z=4$.

$r=$		0·2.	0·4.	0·6.	0·8.	1·0.
ξ	Formula (A)	0·0137566	0·0137419	0·0137172	0·0136836	0·0136406
	,, (B)	0·0137564	0·0137416	0·0137172	0·0136834	0·0136405

TABLE II.

$z=r=$		0·2.	0·4.	0·6.	0·8.	1·0.
ξ	Formula (B)	0·117413	0·087350	0·067835	0·054688	0·045477
	,, (C)	0·117417	0·087348	0·067834	0·054686	0·045476

TABLE III. $\xi = \dfrac{N}{2\pi^2 r^3}$.

r.	$z=0$.	0·2.	0·4.	0·6.
1·0	0·122063	0·09469	0·075971	0·062649
0·8	0·134215	0·10182	0·080307	0·065405
0·6	0·145694	0·10835	0·084106	0·067835
0·4	0·155685	0·11378	0·087350	0·069746
0·2	0·163223	0·11741	0·089389	0·070970

r.	$z=0·8$.	1·0.	2·0.	4·0.
1·0	0·052866	0·045477	0·026022	0·013641
0·8	0·054687	0·046722	0 026297	0·013684
0·6	0·056260	0·047778	0 026520	0·013717
0·4	0·057477	0·048585	0·026685	0·013742
0·2	0·058249	0·049093	0·026785	0 013756

TABLE IV. $\eta = \dfrac{1}{9} - \dfrac{Nz}{\pi^2 r^3}$.

r.	$z=4$.	5.	6.	8.	10.
1·0	0·001986	1292	0906	0514	0331
0·8	1642	1066	0746	0423	0271
0·6	1373	0888	0620	0351	0225
0·4	1176	0760	0530	0300	0192
0·2	1058	6683	0476	0269	0173

10. *Mutual inductances of finite coils.*

(a) Non-overlapping coils.

By definition, N gives the mutual induction between two semi-infinite solid coils of unit winding density, having radii r and unity, the distance of their faces being z. If the radii of the coils are a and b, the separation c, and the winding densities n_1, n_2, then by dimensions the mutual induction is

$$n_1 n_2 a^5 N\left(\frac{c}{a}, \frac{b}{a}\right) \quad \cdots \quad \cdots \quad (39)$$

with $b < a$.

If $b > a$, then from the reciprocal property

$$a^5 N\left(\frac{c}{a}, \frac{b}{a}\right) = b^5 N\left(\frac{c}{b}, \frac{a}{b}\right). \quad \cdots \quad (40)$$

If the coils are hollow, and the inner and outer radii are a_1, a_2 ; b_1, b_2 respectively, then from the laws of combination of mutual inductances, the mutual induction (M) is given by

$$M/n_1 n_2 = a_2{}^5 \left\{ N\left(\frac{c}{a_2}, \frac{b_2}{a_2}\right) - N\left(\frac{c}{a_2}, \frac{b_1}{a_2}\right) \right\}$$

$$- a_1{}^5 \left\{ N\left(\frac{c}{a_1}, \frac{b_2}{a_1}\right) - N\left(\frac{c}{a_1}, \frac{b_1}{a_1}\right) \right\} \quad \cdots \quad (41)$$

When the coils have the same radii (41) becomes (using (40))

$$M/n_1 n_2 = a_2{}^5 N\left(\frac{c}{a_2}, 1\right) - 2a_2{}^5 N\left(\frac{c}{a_2}, \frac{a_1}{a_2}\right) + a_1{}^5 N\left(\frac{c}{a_1}, 1\right). \quad (41a)$$

If in addition, the coils are in contact

$$M/n_1 n_2 = (a_2{}^5 + a_1{}^5) N(0, 1) - 2a_2{}^5 N\left(0, \frac{a_1}{a_2}\right) \quad . \quad (41b)$$

Now let the coils be finite and of lengths $2l_1$, $2l_2$, the distance of their mid-points being h. From the laws of combination of mutual inductances we find

$$M = M(h - l_1 - l_2) + M(h + l_1 + l_2)$$
$$- M(h - l_1 + l_2) - M(h + l_1 - l_2), \quad \cdots \quad (42)$$

in which $M(c)$ is given by (41).

When the coils have the same length

$$M = M(h - 2l) + M(h + 2l) - 2M(h). \quad \cdots \quad (42a)$$

(b) Overlapping coils.

Regard the field inside the outer coil as made up of two portions,

(1) the uniform field calculated by assuming the coil to be part of an infinite coil;

(2) the field due to the polarity of the coil faces.

If M_1, M_2 are the linkages through the second coil due to these two fields, then $M = M_1 + M_2$; M_2 is given by (42) and (41) (no regard being paid to the sign of c), and

$$M_1 = \frac{4}{3}\pi^2 n_1 n_2 k(a_2 - a_1)(b_2{}^3 - b_1{}^3), \quad . \quad . \quad (43)^*$$

k being the length of the overlap.

When the coils have common centres, $h = 0$, and (42) becomes

$$M_2 = 2\{M(l_1 + l_2) - M(l_1 - l_2)\}. \quad . \quad . \quad (42b)$$

If in addition they have the same length $(2l)$,

$$M_2 = 2\{M(2l) - M(0)\} \quad . \quad . \quad . \quad (42c)$$

11. For the purposes of calculation, it is convenient to alter the notation as in the following example.

Let the coils have the following dimensions :—

Outer radii	$a_2 = 10$ cm.,	$b_2 = 4$ cm.
Inner radii	$a_1 = 5$ cm.,	$b_1 = 2$ cm.
Lengths	$2l_1 = 6$ cm.,	$2l_2 = 44$ cm.

Displacement of centres $= h = 21$ cm.

Then since the amount of overlapping is 4 cm., we have from (43)

$$\frac{M_1}{2\pi^2 n_1 n_2} = \frac{2}{3} \times 4 \times 5 \times (4^3 - 2^3) = 746\cdot7.$$

Again,

$h - l_1 - l_2 = c_1 = 4,$	$c_1/a_2 = z_1 = 0\cdot4,$	$c_1/a_1 = z_1{}' = 0\cdot8$
$h + l_1 + l_2 = c_2 = 46,$	$c_2/a_2 = z_2 = 4\cdot6,$	$c_2/a_1 - z_2{}' = 9\cdot2$
$h - l_1 + l_2 = c_3 = 40,$	$c_3/a_2 = z_3 = 4\cdot0,$	$c_3/a_1 = z_3{}' = 8\cdot0$
$h + l_1 - l_2 = c_4 = 2,$	$c_4/a_2 = z_4 = 0\cdot2,$	$c_4/a_1 = z_4{}' = 0\cdot4$

$b_2/a_2 = r_1 = 0\cdot4, \; b_1/a^2 = r_2 = 0\cdot2, \; b_2/a_1 = r_1 = 0\cdot8, \; b_1/a_1 = r_2{}' = 0\cdot4.$

* Maxwell, ' Electricity and Magnetism,' vol. ii. p. 312.

Therefore by (41) and (42), using the notation ξ of the Tables and putting

$$\xi_{pq} \text{ for } \xi(z_p, r_q), \quad \xi'_{pq} \text{ for } \xi(z_p', r_q')$$

$$\frac{M_2}{2\pi^2 n_1 n_2} = a_2^5\{r_1^3(\xi_{11} + \xi_{21} - \xi_{31} - \xi_{41}) - r_2^3(\xi_{12} + \xi_{22} - \xi_{32} - \xi_{42})\}$$

$$- a_1^5\{r_1'^3(\xi'_{11} + \xi'_{21} - \xi'_{31} - \xi'_{41}) - r'_2{}^3(\xi'_{12} + \xi'_{22} - \xi'_{32} - \xi'_{42})\}$$

$$= 10^5\left(-\frac{4^3}{10^3} \times 0\cdot02820 + \frac{2^3}{10^3} \times 0\cdot02978\right)$$

$$- 5^5\left(-\frac{8^3}{10^3} \times 0\cdot03652 + \frac{4^3}{10^3} \times 0\cdot03077\right)$$

$$= -104\cdot4.$$

$$\therefore M = M_1 + M_2 = 2\pi^2 n_1 n_2(746\cdot7 - 104\cdot4) = 12,680 n_1 n_2.$$

12. *Self-inductances.*

Since the self-induction of a coil is the same as the mutual induction between two coincident coils, we have by the method of section 10,

$$L = L_1 + L_2,$$

in which L_1 is the self-induction calculated by assuming the coil to be part of an infinite coil and L_2 are the linkages due to the polar field of the coil.

If the coil has length c, outer radius a, inner radius b, winding density n,

$$L_1 = \tfrac{2}{3}\pi^2 n^2 a^5 z(1-r)^2(1+2r+3r^2), \quad . \quad . \quad (44)$$

in which $z = c/a$, $r = b/a$, and no allowance is made for the space occupied by insulation.

Also L_2 is given by the M_2 of (42 c) in which (41 a) holds, so that, using the present notation,

$$L_2 = 2\{M(c) - M(0)\} . \quad . \quad . \quad . \quad (45)$$

$$M(c)/n^2 = a^5\left\{N(z, 1) - 2N(z, r) + r^5 N\left(\frac{z}{r}, 1\right)\right\} \Bigg\}, \quad (46)$$

$$M(0)/n^2 = a^5\{(1 + r^5)N(0, 1) - 2N(0, r)\}$$

or using the notation ξ, η of the tables,

$$M(c)/2\pi^2 n^2 a^5 = \xi(z, 1) - 2r^3\xi(z, r) + r^5\xi\left(\frac{z}{r}, 1\right)$$

when $z < 4$,

$$M(c)z/\pi^2 n^2 a^5 = \frac{1}{9}(1-r^3)^2 - \eta(z, 1) + 2r^3\eta(z, r) - r^6\eta\left(\frac{z}{r}, 1\right) \Bigg\}. \quad (47)$$

when $z > 4$,

and

$$M(0)/2\pi^2 n^2 a^5 = (1 + r^5)\xi(0, 1) - 2r^3\xi(0, r).$$

When $z > 4$, we obtain an accuracy of 1 in 10,000 if we use

$$L = L_1\left(1 - \frac{\alpha}{z} + \frac{\beta}{z^2} - \frac{\gamma}{z^4}\right), \quad . \quad . \quad . \quad (48)$$

in which α, β, γ are functions of r and are tabulated below.

TABLE V.

r.	α.	β.	γ.
0·0	0·73238	0·33333	0·0953
0·2	0·73699	0·33719	0·0973
0·4	0·75574	0·35579	0·1071
0·6	0·78447	0·39042	0·1306
0·8	0·81718	0·43906	0·1701
1·0	0·84883	0·50000	0·2306

The values of α, β, γ have been calculated from the formulæ

$$\left.\begin{array}{l} q\alpha = 2\{(1 + r^5)\xi(0, 1) - 2r^3\xi(0, r), \\[2mm] q\beta = \dfrac{1}{9}(1 - r^3)^2, \\[2mm] q\gamma = z^2\left\{\eta(z, 1) - 2r^3\eta(z, r) + r^6\eta\left(\dfrac{z}{r}, 1\right)\right\}, \end{array}\right\} \quad . \quad (49)$$

$$q = \frac{1}{3}(1 - r)^2(1 + 2r + 3r^2),$$

with $z = 4$ in the expression for γ. Hence the tabulated values of γ are only correct for $z = 4$. However, for larger values of z, the error in the final result is always less than 1 in 10,000.

The above formulæ fail when $r = 1$, but in this case the coil becomes a thin cylinder, the self-induction of which is

$$L = L_1\left(1 - \frac{8}{3\pi}\frac{1}{z} + \frac{1}{2}\frac{1}{z^2} - \frac{1}{4}\frac{1}{z^4} + \frac{5}{16}\frac{1}{z^6} - \frac{35}{64z^8} + \ldots\right). \quad (50)^*$$

so that for $r = 1$,

$$\alpha = \frac{8}{3\pi}, \quad \beta = \frac{1}{2}, \quad \gamma = \frac{1}{4} - \frac{5}{16z^2} + \frac{35}{64z^4} - \ldots$$

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* Russell, Phil. Mag. vol. xiii. p. 420 (1907); Havelock, Phil. Mag. vol. xv. p. 332 (1908).

13. In order to illustrate the method of working for short coils, take a coil having

$$\text{outer radius} = a = 4 \text{ cm.,}$$
$$\text{inner radius} = b = 2 \text{ cm.,}$$
$$\text{length} = c = 4 \text{ cm.}$$

Then $\quad z = c/a = l,, \qquad r = b/a = 0 \cdot 5.$

By (44) $\qquad L_1/2\pi^2 n^2 a^5 = 0 \cdot 229167.$

By (47 a)

$$M(c)/2\pi^2 n^2 a^5 = \xi(1, 1) - 2(0 \cdot 5)^3 \xi(1, 0 \cdot 5) + (0 \cdot 5)^5 \xi(2, 1),$$
$$= 0 \cdot 045477 - \frac{1}{4} \times 0 \cdot 048216 + \frac{1}{32} \times 0 \cdot 026022,$$
$$= 0 \cdot 034236,$$

$$M(0)/2\pi^2 n^2 a^5 = \left(1 + \frac{1}{32}\right) \times 0 \cdot 122062 - \frac{1}{4} \times 0 \cdot 150930,$$
$$= 0 \cdot 088144.$$

Therefore $\qquad L = L_1 - 2M(0) + 2M(c)$
$$= 2\pi^2 n^2 a^5 (0 \cdot 121351)$$
$$= 2453 \cdot 9 n^2.$$

The Stefan-Weinstein * formula for the same coil gives
$$L = 2459 \cdot 5 n^2,$$

so that the error in using the latter formula for this coil is 0·23 per cent.

14. *Conclusion.*

In applying the formulæ and tables, their range of application should be borne in mind. They are intended to be used only when the inner and outer diameters of the coils differ appreciably ($b/a < 0 \cdot 8$), and when the coil-lengths are not too small ($c/a > 0 \cdot 2$). An exception to this rule is Table V. which (with graphical interpolation) holds for all values of b/a. For coils whose dimensions are outside these limits the usual solenoid or circular filament formulæ are more suitable, the geometric mean distance correction being applied to the channel section.

It should also be noted that no allowance is made for the insulation space of the winding.

Finally, by successive differentiation of the formulæ for the function N, many known formulæ for the mutual induction between solenoids, flat coils, and circles may be obtained.

* Fleming, 'Principles of Electric Wave Telegraphy,' p. 140 (2nd edition).

LIX. *The van der Waals Formula (and the Latent Heat of Vaporization).* By T. CARLTON SUTTON, *B.Sc., Government Research Scholar in the University of Melbourne*[*].

IN the Journal of the Chemical Society, 1914 (p. 734), Applebey and Chapman derive a "formula for the latent heat of vaporization" which gives results in good agreement with those of Mills and Young[†].

The impression given by their paper is that the Mills-Young values are "observed," and may be used as experimental data confirming theoretical results. This is so, only in the sense that the Mills-Young values are "calculated from observed" values of pressure, temperature, and volume by a process very similar to that which Applebey and Chapman themselves employ (see Appendix).

This considerably modifies the inferences that should be drawn from their work.

The chief difference in the processes is that Mills[‡] uses the Biot's formula

$$\log p = A + B\alpha^t + C\beta^t$$

to express the relation between vapour-pressure and temperature, where $A\ B\ C\ \alpha\ \beta$ are five arbitrary constants chosen to suit the measured values of the vapour-pressure, t is the temperature, and p the saturation vapour-pressure; whereas Applebey and Chapman prefer to use a form of van der Waals' equation

$$\left(p + \frac{a}{v^2}\right)(v - b) = Rt,$$

in which b is to be treated as a variable. They find afterwards that b varies uniformly with the temperature. Consequently, the equation may be put in the form

$$\left(p + \frac{a}{v^2}\right)(v - b_c - \gamma\,\overline{t_c - t}) = Rt,$$

where t_c is the critical temperature, $\gamma = \dfrac{db}{dt} = $ constant, and b_c is the value of b at the critical temperature.

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[*] Communicated by Prof. Sydney Young.
[†] Sci. Proc. R. Dublin Soc. 1910, p. 412.
[‡] Journal of Physical Chemistry, 1902, 1905 *et sqq.*

As shown in the Appendix, this leads to the results

$$L = t(v_2 - v_1)\{B \log \alpha \cdot \alpha^t + C \log \beta \cdot \beta^t\}$$

and

$$L = Rt \log \frac{v_2 - b}{v_1 - b} + Rt^2\left(\frac{1}{v_1 - b} - \frac{1}{v_2 - b}\right)\frac{db}{dt} \quad . \quad (B)$$

respectively, where L, v_1 and v_2 are the molecular latent heat, molecular volume of liquid and molecular volume of vapour at temperature t, b is the van der Waals' constant closely connected with the volume actually occupied by the molecule, and R is the gas constant.

The following table compares the results so calculated with such experimental measurements as have been actually made. The latter are meagre, and have been made at the boiling-points (under one atmosphere pressure) only.

	Temp.	L (per grm.) Calculated.		L Obsd.	Date, &c.
		Mills–Young.	Applebey & Chapman.		
Ethyl Ether	34°·5 C.	84·13	87·3	88·4	Wirtz, 1890.
Hexane	68°·0	79·51	79·5	79·4	Mabery and Goldstein, 1902.
Heptane	98°	76·2	76·1	74·0	M. & G., 1902.
Octane	124°·9	70·75	68·4	70·92	Longuinine, 1895.
	125°	70·74	68·4	71·1	M. & G., 1902.
Hexamethylene ...	70°	88·5	86·0	87·3	M. & G., 1902.
Benzene...............	80°·1	95·43	94·8	92·91	Wirtz, 1890.
	80°·35	95·39	94·8	93·45	Schiff, 1886.
Stannic Chloride ...	112°·5	31·0	30·6	30·53	Andrews, 1848.
Methyl Formate ...	32°·9	113·4	118·8	115·2	Berthelot and Ogier, 1881.
	32°·5	113·52	118·9	110·45	Brown, 1903.
Ethyl Formate	54°·2	97 04	95·8	100·4	B. & O., 1881.
	54°·2	97·04	95·8	100·1	Brown, 1903.
	53°·5	97·18	96·0	92·15	Schiff, 1886.
Propyl Formate ...	81°·2	87·19	88·4	85·25	Schiff, 1886.
	81°·2	87·19	88·4	90·36	Brown, 1903.
Methyl Acetate......	57°·3	99·06	105·3	93·95	Schiff, 1886.
	57°·3	99·06	105·3	98·26	Brown, 1903.
Ethyl Acetate	73°·1	86·88	88·6	84·28	Wirtz, 1890.
	74°·0	86·76	88·5	105·0	Schall, 1884.
	77°·0	86·27	88·0	83·1	Schiff, 1886.
	77°·3	86·22	88 0	88·37	Brown, 1903.
Propyl Acetate......	102°·3	79·44	80·7	77·3	Schiff, 1886.
	102°·3	79·44	80·7	80·45	Brown, 1903.
Methyl Propionate .	80°·0	87·07	88·6	84·15	Schiff, 1886.
	78°·95	87·26	88·8	89·0	Brown, 1903.
Ethyl Propionate...	98°·7	79·4	79·8	77·1	Schiff, 1886.
	99°·2	79·33	79·7	80·3	Brown, 1903.
Methyl Butyrate ...	93°	79·0	81·6	86·0	Schall, 1884.
	102°·3	77·40	80·0	77·25	Schiff, 1886.
	102°·5	77·36	80·0	79·75	Brown, 1903.
Methyl Isobutyrate.	92°·5	75·93	75·6	75·5	Schiff, 1886.
	92°·4	75·95	75·6	79·0	Brown, 1903.

The modified van der Waals' formula

$$\left(p + \frac{a}{v^2}\right)(v - b - \gamma\delta t) = \mathrm{R}t,$$

where $\qquad \gamma = \dfrac{db}{dt} = \text{constant},$

leads to results very close to the measured results. In many ways it is to be preferred to the Biot's formula

$$\log p = \mathrm{A} + \mathrm{B}\alpha^t + \mathrm{C}\beta^t.$$

(1) It contains three adjustable constants, whereas Biot's formula contains five.

(2) Each of these three constants has a physical significance.

(3) The agreement with the measured values of p, v and t is very close—the discrepancies being of the same order of magnitude as when Biot's formula is used.

(4) The derived equation (B) gives values of the latent heat of vaporization in satisfactory agreement with the measured values (*e. g.* at the boiling-point under one atmosphere pressure—see Table), whereas Bakker, using the unmodified van der Waals' equation, obtained results 20 per cent. too low[*].

(5) The tables in Applebey and Chapman's paper (pp. 739–742) show that the agreement between the two series of calculated latent heats is still better at higher temperatures.

The fact that $\dfrac{db}{dt}$ is *found* to be constant, suggests that the molecule expands uniformly with increase of temperature.

[A uniformly expanding atom has been assumed by Schott in the Adams' Prize Essay for 1908[†], and by Richards in some researches published in the *Zeits. Phys. Chem.* xlii. and subsequent vols.]

Applebey and Chapman remark (p. 742–3) " for halogen derivatives " of benzene " the calculated values are all much too high, the mean percentage differences ...... for chlorobenzene, bromobenzene, and iodobenzene being respectively 3·22, 5·54, 5·32." There are no experimental results with which to compare these two series of calculated values. It seemed desirable, therefore, to obtain Mill's constant[‡], μ', for each of these substances.

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[*] Bakker, *Zeits. Phys. Chem.* 1895, p. 519.
[†] Electromagnetic Radiation (Schott), Camb. Univ. Press, 1912.
[‡] See 'Journal of Physical Chemistry,' 1905 and 1909.

Chlorobenzene.

Temperature.	Mill's Constant.		
	Calculated by Biot's formula.		Calculated by Applebey's formula.
	Calc. 1905.	Recalc. from revised data 1909.	
130° C.	79·46	79·9	85·9
160°	80·83	80·9	85·6
190°	81·34	81·5	84·5
220°	81·84	82·2	83·9
240°	83·06	82·8	84·0
270°	84·93	82·5	85·4
Bromobenzene.			
100° C.	56·93	...	59·8
150°	54·10	54·6	59·6
180°	54·98	55·0	59·6
210°	55·9	55·7	59·2
230°	56·25	56·0	58·7
250°	56·44	55·8	58·8
260°	56·92	56·1	58·7
270°	57·15	56·2	58·6
Iodobenzene.			
190° C.	41·87	42·9	45·9
220°	43·64	43·5	46·0
250°	44·38	43·6	46·5
270°	45·10	43·2	46·9

Mills has twice calculated the values of μ', employing Biot's formula to represent the connexion between saturation-pressure and temperature. The calculations of 1905 show irregularities in the values obtained in these same cases, chlorobenzene, bromobenzene, and iodobenzene. The recalculations of 1909, based on Young's revised data, show irregularities that are smaller, but are still much greater than those given by other substances. When the modified van der Waals' equation is used, these irregularities still occur. It will be seen that they are smaller than in the previous cases, though only slightly so. What seems more important is the fact that, in general, maximum values obtained by means of Biot's formula correspond to minimum values obtained by the van der Waals' relation, and so on. This suggests that the error is due to some change in the liquids not accounted for by either of the formulæ.

It seems therefore that in the case of these non-associated

liquids, the differences between the two series of calculated values of latent heat are quite as likely to be due to a divergence of Biot's formula from the facts as to such a divergence of the modified van der Waals' relation.

Consequently it will be seen that this modified van der Waals' relation, and the derived expression (B) for the latent heat of vaporization, hold good for *all* the non-associated liquids examined and for *none* of the associated liquids ; hence the agreement between the two series of calculated latent heats, and the variations in the value of Mills' constant (see above) give delicate tests of association in a liquid.

My thanks are due to Professor Young for supplying some data I had overlooked, and for kindly offering to read the proofs of this paper.

The University,
  Melbourne.

Appendix.

In the following it is shown in detail that the methods of calculation used by Mills-Young and by Applebey-Chapman are essentially the same.

The data employed in the Mills-Young and the Applebey-Chapman calculations are the measurements of the vapour-pressure and the vapour-density of thirty-two pure liquids made by or under the direction of Dr. Sydney Young. These have been collected and revised, and are published in the Scientific Proceedings of the Royal Dublin Society, 1910, pp. 412–443. With them appear Dr. Mills' series of calculated latent heats that we are about to discuss.

In each case the process of reduction has consisted of—

(1) Finding some formula connecting the temperature with either the vapour-pressure or the specific volume of the saturated vapour. Determining the constants of this formula over a range extending to the critical temperature.

(2) Differentiating this formula and substituting the value of $\frac{dp}{dt}$ so found in the Clausius-Clapeyron relation

$$L = t(v_2 - v_1)\frac{dp}{dt},$$

where v_2 and v_1 are the molecular volume of vapour and liquid respectively, t the absolute temperature, p the saturation-pressure, and L the molecular latent heat of vaporization.

(1) For the vapour-pressure formula, Mills[*] has chosen Biot's form

$$\log p = \mathrm{A} + \mathrm{B}\alpha^t + \mathrm{C}\beta^t, \quad . \quad . \quad . \quad . \quad . \quad (a)$$

involving five arbitrary constants.

Applebey and Chapman prefer to use a form such as van der Waals' equation (J. C. S. 1914, p. 734),

$$\left(p + \frac{a}{v^2}\right)(v - b) = \mathrm{R}t,$$

but treat b as a variable (p. 735). Later (p. 736) they find that $\dfrac{db}{dt}$ is a constant, and is to be chosen to suit the data (see method p. 737).

This is equivalent to employing the three-constant formula

$$\left(p + \frac{a}{v^2}\right)\left(v - b - \frac{db}{dt}\,\delta t\right) = \mathrm{R}t, \quad . \quad . \quad . \quad (b)$$

where a, b, and $\dfrac{db}{dt}$ are adjustable constants and R is the gas constant, b is the value of the van der Waals' constant at the critical temperature, and δt the difference between the critical temperature and the absolute temperature considered.

The constants of the formulæ (a) and (b) are chosen so as to suit the same series of measurements—that is to say, so that their graphs may agree as closely as possible with the experimental graph. They are, therefore, the same relation expressed in different forms.

(2) By differentiating to obtain $\dfrac{dp}{dt}$, and substituting its value in the Clausius-Clapeyron relation, Mills gets

$$\mathrm{L} = t(v_2 - v_1)\{\mathrm{B}\log\alpha\,.\,\alpha^t + \mathrm{C}\log\beta\,.\,\beta^t\},$$

while Applebey and Chapman by an ingenious but mathematically similar process (pp. 735–6) obtain

$$\mathrm{L} = \mathrm{R}t\log\left(\frac{v_2 - b}{v_1 - b}\right) + \mathrm{R}t^2\left(\frac{1}{v_1 - b} - \frac{1}{v_2 - b}\right)\frac{db}{dt}.$$

These two formulæ are derived from relations which approximately represent the same experimental results, by means of the same mathematical processes; and should, therefore (if the approximation is good), give concordant values of L.

[*] Journal of Physical Chemistry, 1902, 1904, &c.

Applebey and Chapman obtain (p. 737) the value of $\dfrac{db}{dt}$ by applying the law of rectilinear diameters, and the relation

$$\left(\frac{\delta p}{\delta t}\right)_c = \frac{2R}{v_c},$$

where the suffix c denotes that the measurement is made at the critical point.

Mills, on the other hand, uses the law of rectilinear diameters to obtain the critical constants, chooses the constants of Biot's formula to fit the values so found, and then shows that the result

$$\left(\frac{\delta p}{\delta t}\right)_c = \frac{2R}{v_c}$$

is true—a process equivalent mathematically to that used by Applebey and Chapman.

LX. *The Boiling-Points and Critical Temperatures of Homologous Compounds.* *By* ALLAN FERGUSON, *D.Sc. (Lond.), Assistant Lecturer in Physics in the University College of North Wales, Bangor*[*].

THE present communication explains a new empirical formula which appears to represent the relation between the boiling-points and molecular weights of the normal paraffins with considerable accuracy over a wide range, and also establishes, for the same series, empirical formulæ showing the relation between critical temperature and chemical constitution—a relation which does not, hitherto, appear to have attracted very much notice.

It would serve no useful end to disturb the dust which has collected over formulæ more than a generation old : in discussing previous results it will be sufficient for our purposes to consider the boiling-point equations proposed by Walker [†], by Ramage [‡], and by Young [§].

Walker's formula is of the type

$$\theta = aM^b, \qquad \ldots \ldots \ldots \text{(i.)}$$

where θ is the *absolute* boiling-point, M the molecular weight,

and a and b are constants (for the normal paraffins $a = 37\cdot38$, $b = 0\cdot5$. The boiling-points in this, and in all other cases considered, are supposed to be measured at a pressure of 760 mm.).

This formula represents the observed facts with fair accuracy over a limited range, but does not lend itself well to extrapolation. The reason lies in the fact that the formula, as is obvious, assumes a *linear* relation between log θ and log M, which is by no means the case, as the graph of these quantities shows a slight, but quite distinct, curvature. In this case, therefore, as in all other cases in which a straight line is assumed to coincide with a limited portion of a curve of slight curvature, the agreement between calculated and observed quantities is very good over the mid-portion of the range chosen, but the differences become more and more marked the further one extrapolates beyond either the upper or lower limit of the range chosen.

The formula given by Ramage,

$$\theta = a\left[M(1-2^{-n})\right]^{\frac{1}{2}}, \quad \ldots \quad \text{(ii.)}$$

where a is Walker's constant, and n the number of carbon atoms in the molecule, gives notably improved results for the lower paraffins. But above decane or thereabouts, the factor 2^{-n} becomes negligible, and the formula then becomes identical with Walker's, equally implying a linear relation between log θ and log M, which relation, as is seen by the curve between these quantities, is only approximately fulfilled. From $n = 14$ onwards, the difference between theory and experiment becomes steadily greater.

The formula proposed by Young is of a different type. If Δ be the *difference* between the boiling-point θ of any homologue and that next above it in the series, then

$$\Delta = \frac{c}{\theta d \sqrt{\theta}}, \quad \ldots \quad \ldots \quad \text{(iii.)}$$

where for the normal paraffins (and for certain other series), $c = 144\cdot86$ and $d = \cdot0148$. Thus the boiling-point of any paraffin can be calculated, provided that of the homologue next below it be known. This restriction apart, the formula gives very consistent results, and the observed and calculated results do not show, at the upper and lower limits of the range considered, that tendency to a gradually increasing divergence so characteristic of those formulæ which assume approximate coincidence between a straight line and a curve.

It should be noticed in passing, as we shall have need to use the principle later, that equation (iii.) is really a differential equation. Young's Δ is really the change in

θ per unit change in n, and (iii.) may therefore be written

$$\frac{d\theta}{dn} = \frac{c}{\theta d \sqrt{\theta}}, \quad \cdots \cdots \quad \text{(iv.)}$$

if we treat n as a continuous variable. This equation can—theoretically—be integrated, yielding a relation between θ and n which could then be compared with those of Ramage and of Walker. Unfortunately the resulting integral, though apparently simple in form, does not integrate in terms of any of the simple functions, and the series-form into which it does integrate is somewhat unwieldy to handle *.

It will be seen that in Walker's formula θ is assumed to be proportional to a definite power of M; in the formula now to be proposed a similar relation is assumed to exist between the *logarithms* of θ and of M—that is

$$\log \theta = k(\log M)^s, \quad \cdots \cdots \quad \text{(v.)}$$

or, what amounts to the same thing,

$$\theta = M^{k(\log M)^{s-1}}. \quad \cdots \cdots \quad \text{(vi.)}$$

When θ is measured on the absolute scale, and logarithms are taken to the base 10, we obtain for the normal paraffins $k = 1 \cdot 929$ and $s = \cdot 4134$. These values for the constants k and s hold with considerable accuracy over the range $n = 4$ to $n = 17$, and were obtained by treating the observed boiling-points over this range by the method of least squares. The last two columns in Table I.† show the boiling-points as

TABLE I.

Paraffin.	Boiling-Point (Obs.).	Walker.		Ramage.		Young.		Ferguson.	
		Calc.	Diff.	Calc.	Diff.	Calc.	Diff.	Calc.	Diff.
$C_4H_{10}\cdots$	274·0	...	...	275·6	+1·6	272·6	−1·4	274·7	+0·7
$C_5H_{12}\cdots$	309·3	...	...	312·2	+2·9	309·4	+0·1	310·2	+0·9
$C_6H_{11}\cdots$	342·0	...	...	343·9	+1·9	342·0	+0·0	341·9	−0·1
$C_7H_{16}\cdots$	371·4	373·8	+2·4	372·3	+0·9	371·3	−0·1	370·7	−0·7
$C_8H_{18}\cdots$	398·6	399·1	+0·5	398·3	−0·3	398·1	−0·5	397·2	−1·4
$C_9H_{20}\cdots$	422·5	422·9	+0·4	422·5	+0·0	422·9	+0·4	421·8	−0·7
$C_{10}H_{22}$.	446·0	445·5	−0·5	445·2	−0·8	445·9	−0·1	444·8	−1·2
$C_{11}H_{24}$.	467·0	466·8	−0·2	466·8	−0·2	467·4	+0·4	466·5	−0·5
$C_{12}H_{26}$.	487·5	487·2	−0·3	487·3	−0·2	487·7	+0·2	487·0	−0·5
$C_{13}H_{28}$.	507·0	507·3	+0·3	507·0	+0·0	506·8	−0·2	506·4	−0·6
$C_{14}H_{30}$.	525·5	526·0	+0·5	526·0	+0·5	525·0	−0·5	525·1	−0·4
$C_{15}H_{32}$.	543·5	544·1	+0·6	544·2	+0·7	542·3	−1·2	542·9	−0·6
$C_{16}H_{34}$.	560·5	561·9	+1·4	561·9	+1·4	558·9	−1·6	560·2	−0·3
$C_{17}H_{36}$.	576·0	...	...	579·0	+3·0	574·7	−1·3	576·4	+0·4

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* For assistance in elucidating the properties of this integral I am indebted to the friendly counsel of Mr. G. B. Mathews.

† The observed boiling-points are those given by Young, Phil. Mag. *l. c.*

calculated from equation (v.) and the differences between the observed and calculated values. The remaining columns show the results of similiar computations using equations (i.), (ii.), and (iii.).

A fair idea may be obtained of the relative accuracy of the various formulæ by computing the average error, regardless of sign. Thus

for range $n = 7$ to $n = 16$, average error, $W = 0^{\circ}\cdot71$,

for range $n = 4$ to $n = 17$ $\begin{cases} \text{average error, } R = 1^{\circ}\cdot03, \\ \quad,, \qquad,, \quad Y = 0^{\circ}\cdot58, \\ \quad,, \qquad,, \quad F = 0^{\circ}\cdot64. \end{cases}$

Thus it appears that, over the range taken, the new formula is more accurate than either (i.) or (ii.), and, whilst having the advantage of not being a difference formula, is only slightly less exact than that of Young. Further, the differences between the calculated and observed values are much the same in magnitude at any point of the range.

We now turn to the consideration of the relation between critical temperature and constitution. Granted sufficient exact experimental data, it would not be a difficult task to find directly various empirical relations connecting critical temperature and molecular weight in the normal paraffins. In the present paper an indirect method is followed, which will be seen in the sequel to lead to results of a fairly high order of accuracy, while several interesting relationships will be elucidated by the way, which would be obscured by the direct method of attack.

It has long been known that different substances are approximately in "corresponding states" as far as temperature is concerned, when at their boiling-points (under normal pressure) ; were this exactly true, the ratio of the critical temperature to the boiling-point, when measured on the absolute scale, would be a constant for all substances. Now while it is the case that this ratio does not vary very greatly for substances whose boiling-points are so diverse as those of oxygen and aniline, there is, nevertheless, a slight variation, and this variation is, for the normal paraffins, a perfectly regular one. Calling the ratio θ_c/θ for any given paraffin R, and the corresponding number of carbon atoms in the molecule n, it can be shown graphically that the relation between $\log R$ and $\log n$ is very accurately linear, leading therefore to the relation

$$R n^g = h, \quad \ldots \quad \ldots \quad \text{(vii.)}$$

where g and h are constants. For the normal paraffins the

values of these constants, as determined from the graph between $\log R$ and $\log n$, are $g = \cdot 120$ and $h = 1 \cdot 841$. The closeness with which equation (vii.) fits the observed values is exhibited in Table II. below.

TABLE II.*

n.	R (observed).	R (calculated).	Per cent. error.
1	1·764	[1·841]	......
2	1·694	1·693	−0·06
3	1·623	1·614	−0·56
4	......	1·559	−0·38
5	1·520	1·517	−0·20
6	1·485	1·481	−0·27
7	1·454	1·457	+0·21
8	1·427	1·434	+0·50
9	......	1·415	+0·14
10	1·402	1·396	−0·43

Average percentage difference neglecting sign $= 0 \cdot 33$ per cent.

It seems therefore that, apart from the first member of the series, which, as usual, is anomalous, equation (vii.) fits the observed values very exactly. It can easily be deduced from (vii.) that if R_n and R_{n+1} be two successive values of R for two paraffins having n and $n+1$ carbon atoms in the molecule, then

$$\frac{R_n}{R_{n+1}} = \left(1 + \frac{1}{n} \right)^g, \quad \cdots \quad \text{(viii.)}$$

bringing out quite clearly the observed facts that the value of R decreases as n increases, but at a decreasing rate. In fact, if (vii.) can be assumed to hold over any wide range, (viii.) shows that for large values of n the corresponding values of R tend to become equal.

Writing (vii.) in the form

$$\theta_c n^g = h\theta, \quad \cdots \quad \cdots \quad \text{(ix.)}$$

it is clear that θ can be eliminated between (ix.) and any of the various formulæ [(i.), (ii.), (iii.), and (v.)] proposed to represent the relation between boiling-point and constitution. We thus obtain empirical formulæ for θ_c which will vary in form according to the particular boiling-point relation chosen.

Thus, eliminating θ between (ix.) and Walker's equation (i.)

* The observed values of R are given by Young, 'Stoichiometry,' p. 183.

we obtain, after giving to the various constants their numerical values,

$$\theta_c = \frac{68 \cdot 80 \ \sqrt{M}}{n^{\cdot 120}}. \quad . \quad . \quad . \quad . \quad \text{(x.)}$$

Similarly, using Ramage's equation (ii.), we find that

$$\theta_c = \frac{68 \cdot 80}{n^{\cdot 120}} [M(1 - 2^{-n})]^{\frac{1}{2}}. \quad . \quad . \quad \text{(xi.)}$$

As Young's formula is a difference formula, a different method has to be followed in effecting the elimination. Assuming n to be a continuous variable and differentiating (ix.) with respect to n, we have

$$h \frac{d\theta}{dn} = n^g \frac{d\theta_c}{dn} + \theta_c g n^{g-1}. \quad . \quad . \quad . \quad \text{(xii.)}$$

Eliminating $\frac{d\theta}{dn}$ between (xii.) and (iv.), writing $\frac{d\theta_c}{dn}$ as Δ_c in accordance with Young's notation, and substituting the numerical values of the constants in the resulting equation, we obtain

$$\Delta_c = \frac{1}{n^{\cdot 120}} \left\{ \frac{266 \cdot 7}{\theta^{\cdot 0148} \sqrt{\theta}} - \frac{\cdot 120 \, \theta_c}{n^{\cdot 88}} \right\}. \quad . \quad . \quad \text{(xiii.)}$$

Δ_c is the difference between the critical temperature of any given paraffin and that of its homologue next higher in the series; θ_c, θ, and n refer to the given paraffin. So that, knowing the boiling-point and critical temperature of any given paraffin, the critical temperature of its next higher homologue can be calculated from (xiii.). In fact, the method of use of (xiii.) for calculating critical temperatures is strictly analogous to that of (iii.) for calculating boiling-points.

If we take equation (v.) as our boiling-point formula, then, taking logarithms of (ix.), and eliminating $\log \theta$ between this and (v.), we find that

$$\log \theta_c = \log h + k (\log M)^s - g \log n, \quad . \quad . \quad \text{(xiv.)}$$

a relation which is equivalent to

$$\theta_c = \frac{h M^{k(\log M)^{s-1}}}{n^g}. \quad . \quad . \quad . \quad . \quad \text{(xv.)}$$

Substituting the numerical values of the constants in (xiv.),

which is the most convenient form for computation, we have

$$\log \theta_c = \cdot 2650 + 1 \cdot 929 \, (\log M)^{\cdot 4134} - \cdot 120 \log n, \quad \text{(xvi.)}$$

as the empirical equation which gives the relation between the critical temperature and molecular weight of the normal paraffins.

It now remains to compare the values calculated from formulæ (x.), (xi.), (xiii.), and (xvi.) with the observed values of θ_c. Unfortunately the data for critical temperatures, like those for boiling-points, are of very different value, and one has either to adopt certain more or less arbitrary canons of selection or rejection, or to take the average value of the various figures given for any one substance by different experimenters—a process about as likely to result in the true critical temperature as the averaging of half-a-dozen slightly erratic public clocks is to result in Greenwich mean time.

In comparing, therefore, the calculated and observed values of θ_c, I have restricted myself to the accurately-determined values for pentane, hexane, heptane, and octane given in Young's Royal Dublin Society paper*. The comparison is shown in Table III. below.

TABLE III.

Paraffin.	θ_c. obs.	Calc. from (x.).	Diff.	Calc. from (xi.).	Diff.	Calc. from (xiii.).	Diff.	Calc. from (xvi.).	Diff.
C_5H_{12}...	470·2	[481·2]	+11·0	473·7	+3·5	...	...	470·7	+0·5
C_6H_{14}...	507·8	[514·6]	+6·8	510·6	+2·8	508·3	+0·5	507·6	−0·2
C_7H_{16}...	539·9	544·8	+4·9	542·6	+2·7	541·2	+1·3	540·3	+0·4
C_8H_{18}...	569·2	572·5	+3·3	571·4	+2·2	569·7	+0·5	569·6	+0·4
C_9H_{20}...	...	597·8	...	597·3	...	596·0	...	596·5	
$C_{10}H_{22}$ ·	··	622·2	...	621·9	...	...	...	621·2	

The first two values in the third column are bracketed, since Walker's boiling-point formula only has reference to the paraffins between C_7H_{16} and $C_{16}H_{34}$. It will be seen that the values given by formula (xiii.) deduced from Young's boiling-point equation are in close agreement with the experimental numbers, and that the values calculated from equation (xvi.), which is deduced from the boiling-point

* Proc. R. D. S. xii. 31. p. 374 (1910).

equation proposed by the present writer, agree still more exactly with the observed values. Making due reservation for the paucity of the experimental data, it would seem that (xvi.) can be used with some confidence to calculate the critical temperatures of the higher members of the series of normal paraffins.

Proceeding on similar lines to those followed in deducing boiling-point formulæ for the paraffins, it would be possible to obtain empirical equations for other homologous series. But it is perhaps of more interest to consider certain of these series as derived from the paraffins by substitution, thus obtaining some insight into the question of replacement values. Taking the primary alkyl bromides as an example, defining the term "replacement value" as meaning the difference between the boiling-point of the paraffin and that of the corresponding bromide, and denoting it by ρ, we find that the graph between $\log \rho$ and $\log n$ is very closely linear. This leads at once to the relation

$$\rho n^{.436} = 187 \cdot 5,$$

or since

$$\rho = \theta_B - \theta_P,$$

we may write

$$\theta_B = \theta_P + \frac{187 \cdot 5}{n^{.436}}, \quad . \quad . \quad . \quad \text{(xvii.)}$$

where n as usual is the number of carbon atoms in the molecule (the numerical values of the constants were read off directly from the graph). From (xvii.), therefore, we may calculate at once the boiling point of a given primary alkyl bromide, if we know that of the corresponding paraffin. The agreement between the observed and calculated values is shown in Table IV. below.

TABLE IV.*

Bromide.	θ_P obs.	θ_B obs.	θ_B calc.	Difference.
C_3H_7Br	228·0	343·8	344·1	+0·3
C_4H_9Br	274·0	374·0	376·0	+2·0
$C_5H_{11}Br$......	309·3	402·5	402·2	−0·3
$C_6H_{13}Br$......	342·0	429·0	427·8	−1·2
$C_7H_{15}Br$......	371·4	452·0	451·7	−0·3
$C_8H_{17}Br$......	398·6	474·0	474·3	+0·3

Average difference regardless of sign $= 0° \cdot 73$.

* Observed values from Young, Phil. Mag. *l. c.*

It is of interest to see whether analogous formulæ can be applied to those series in which the influence of association is manifest—the primary alkyl alcohols, for example. If the graph between $\log \rho$ and $\log n$ be plotted for this series, it will be seen that whilst the relation between $\log \rho$ and $\log n$ is still approximately linear, the points are scattered rather irregularly about the line passing through their mean position. Calculating for this line, we find that

$$\theta_A = \theta_P + \frac{331 \cdot 1}{n^{\cdot 7456}}, \quad . \quad . \quad . \quad . \quad . \quad \text{(xvii.)}$$

giving the boiling-point of the alcohol (θ_A) in terms of that of the corresponding paraffin (θ_P). The results are shown in Table V.

<div align="center">TABLE V.*</div>

Alcohol.	θ_P obs.	θ_A obs.	θ_A calc.	Difference.
C_3H_7OH ..	228·0	370·2	374·0	+3·8
C_4H_9OH ...	274·0	389·9	391·8	+1·9
$C_5H_{11}OH$ ...	309·3	411·0	409·0	−2·0
$C_6H_{13}OH$ ...	342·0	431·0	429·0	−2·0
$C_7H_{15}OH$ ...	371·4	449·0	449·0	±0·0
$C_8H_{17}OH$ ...	398·6	464·0	468·8	+4·8
$C_9H_{19}OH$ ...	422·5	486·5	486·8	+0·3
$C_{10}H_{21}OH$...	446·0	504·0	505·5	+1·5

<div align="center">Average difference regardless of sign $= 2° \cdot 04$.</div>

Whilst, therefore, the equation for the bromides is in close agreement with the observed facts, that for the alcohols shows much greater divergences. A similar divergence has been noted by Young, who, using equation (iii.), has calculated values for Δ for each of the series considered above. In the case of the bromides the average difference regardless of sign between the observed and calculated values of Δ is, over the range taken, $1° \cdot 25$. In the case of the alcohols the average difference between the observed and calculated values of Δ is $4° \cdot 28$. Thus, while the average values of the errors in Δ are considerably larger than those in the formulæ (xviii.) and (xvii.), the *ratios* of the errors are very approximately the same, for in each case the error for the alcohols is about three times the corresponding error for the bromides.

<div align="center">* Observed data from Young, *l. c.*</div>

Summary.

(1) A boiling-point formula is proposed for the normal paraffins

$$\log \theta = 1 \cdot 929 \, (\log M)^{\cdot 4134} \quad . \quad \cdot \quad . \quad . \quad (\alpha)$$

which covers the range from $n = 4$ to $n = 17$ with an average error of $0° \cdot 64$.

(2) An equation

$$\frac{\theta_c}{\theta} \, n^{\cdot 120} = 1 \cdot 841 \, . \quad . \quad . \quad . \quad . \quad (\beta)$$

is shown to hold for the normal paraffins between ethane and decane with an average error of $0 \cdot 33$ per cent.

(3) By eliminating θ between (β) and any of the various boiling-point formulæ, empirical equations are obtained for the critical temperatures of the normal paraffins. In particular, the equation

$$\log \theta_c = \cdot 2650 + 1 \cdot 929 \, (\log M)^{\cdot 4134} - \cdot 120 \log n \quad . \quad (\gamma)$$

is shown to be in very close agreement with the observed facts.

(4) The boiling-points of the primary alkyl bromides are connected with those of the corresponding paraffins by the equation

$$\theta_B = \theta_P + \frac{187 \cdot 5}{n^{\cdot 436}}, \, . \quad . \quad . \quad . \quad (\delta)$$

the mean error over the range $n = 3$ to $n = 8$ being $0° \cdot 73$.

(5) A similar formula for the primary alcohols, viz.:

$$\theta_A = \theta_P + \frac{331 \cdot 1}{n^{\cdot 7456}}, \, . \quad . \quad , \quad . \quad . \quad (\epsilon)$$

gives the boiling-points of the alcohols over the range $n = 3$ to $n = 10$ with an average error of $2° \cdot 04$.

The writer hopes, with wider data, to extend these formulæ, especially as regards critical temperatures, to other allied series.

University College of North Wales,
    Bangor.
    January 1914.

LXI. *On a New Form of Sulphuric-Acid Drying-Vessel.*
By the Earl of Berkeley, *F.R.S., and* E. G. J.
Hartley, *B.A.*[*]

IN the course of a prolonged series of measurements of the
vapour pressure of aqueous solutions, some of which
have already been published [†], the method employed has
been to saturate a current of dry air with the vapour of the
solution and pure solvent respectively. The problem of
drying the air-current has thus arisen, and some experi-
ments to determine the relative efficiency of phosphorus
pentoxide and sulphuric acid as desiccating agents seem to
be worth recording, since comparatively few quantitative
results on this subject appear to have been published [‡].

Our experiments were designed to throw light on two
separate points, and proof was thereby obtained that :—

(1) Sulphuric acid is capable of drying air as completely
as phosphorus pentoxide, at least to the extent that is
required in this class of work.

(2) By employing suitable apparatus it is not necessary to
bubble [§] the air through the acid, but only to lead it over its
surface ; thus avoiding both the risk of introducing acid
spray into the air-stream and uncertain changes in the volume
of the air-current. In vapour-pressure measurements by
this method the latter source of error is of considerable
importance ‖.

In addition to the foregoing it was shown that the vapour
pressure of the sulphuric acid itself, to which Mr. J. J Manley
has called attention ¶, is too small to be of importance.

For these experiments a new form of phosphorus-pent-
oxide vessel was devised having some points of advantage
over the usual tube ; we give a description of it as it may be
of use to others. This vessel is shown in figs. 1 and 2 ;
legs are sealed in at the sides at *a*, thus enabling it to
stand on the balance or elsewhere without support; it is fitted
with a ground-on cap *b* and a ground-on detachable mercury
cup *c*. It may be mentioned here that we have found this

mercury-cup joint very satisfactory for vapour-pressure work up to 30° C., where the pressure of the mercury is still insignificant.   There have been no signs of leak even when the joint has been under water, but in the latter case it is advisable to put rubber lubricant on the ground glass that holds the cup ; this lubricant is dissolved off with petrol before weighing the vessel.

The most convenient way of filling the vessel is to pass the inlet tube just through a rubber plug of the right size to fit the mouth of the phosphorus-pentoxide bottle ; on inverting the bottle and gently tapping, the drying agent runs freely into the vessel, thus avoiding exposure to external moisture.   For a large number of experiments it is better

Fig. 3.
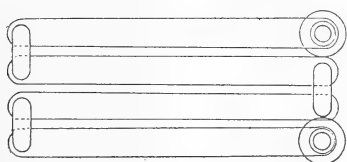
Fig. 4.
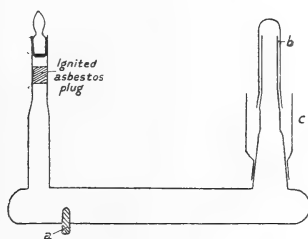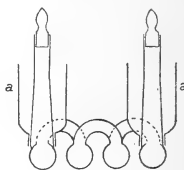
Fig. 1.

Fig. 2.

to purchase stoppered bottles, each containing about one charge of the pentoxide, and keep them over sulphuric acid in a desiccator.

After filling, the vessel was heated to about 240° C. in a stream of dry ozonized air until ozone issued freely.   By this treatment Mr. Manley [*] has shown that the lower oxides of phosphorus are completely oxidized [†].

The sulphuric-acid vessel is shown in figs. 3 and 4 ; it is fitted with detachable mercury cups, and an inverted U tube

[*] Private communication.

[†] It should be noted that of the various samples of phosphorus pentoxide tried, only Kahlbaum's was treated successfully in this way.   All the others contained such a large proportion of impurities that even after many hours' run practically all the ozone in a rapid current was absorbed.

joins it to the pentoxide tube. The four horizontal branches (each 22 cm. long with an external diameter of 2 cm.) are about half filled with acid, which is thus contained in four separate compartments, so that the moisture from the wet-air stream is nearly all absorbed in the first compartment. A long series of experiments, which need not be detailed here, have proved that with such a vessel containing 70 c.c. of acid (10 c.c. in the first compartment), 20 c.c. of water can be abstracted from an air-current without allowing any to pass —or put in another way, air saturated with moisture at 30° C. will be completely dehydrated, although passed for 5 days at a rate such that 0·15 gramme of water is taken up per hour.

In the first experiment, a current of moist air was drawn through a soda-lime tube * to remove the greater part of the moisture and then through a Winkler sulphuric-acid drying-vessel of large size connected to the pentoxide tube. The air-bubbles were formed in the Winkler at the rate of 50 in 14 seconds. After 52 hours the pentoxide tube was weighed and had gained ·0010 gramme. As no special precautions had been taken to dry the tube connecting the Winkler to the pentoxide, the same experiment was repeated immediately after the above weighing, and the air passed for 160 hours. The gain in weight of the phosphorus pentoxide was now only ·0002 gramme, showing that the sulphuric acid had allowed practically no moisture to pass by.

In all these experiments the pentoxide tube was weighed against a glass counterpoise of about the same external area, and, before weighing, both vessels were washed and dried in as near a similar manner as possible, the weighings being reduced to a vacuum.

In the next experiment the Winkler was replaced by the new form of sulphuric-acid vessel. After a week's run, when about 600 litres of air had passed, the sulphuric acid had absorbed 5·52 grammes of water while the pentoxide tube had gained only ·0001 gramme.

Further evidence of the efficacy of this form of vessel is found in a great number of experiments in which air was passed over water, in a weighed vessel, and then over the sulphuric acid. The loss in the former should equal the gain in the latter. Without entering into lengthy details the following gives some idea as to the magnitudes involved— the vessels were similar to those described by us in Proc. Roy. Soc. A. vol. lxxvii. p. 158 (1906).

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* Cp. note on page 613.

In a run at 30° C. nearly 7 grammes of water was passed over 23 c.c. of acid (4 c.c. in the first branch) at the rate of ·11 gramme per hour without any loss ; the spent acid in the first (inlet) branch was then replaced by 4 c.c. of fresh acid and the run continued at a rate of ·075 gramme per hour until another 7 grammes had passed—again there was no loss.

The advantages of the new form over the Winkler seem therefore to be as follows :—

(1) There is no constriction in the air-current.

(2) There is no danger from sulphuric-acid spray.

(3) Even after a somewhat prolonged use the drying agent is still effective; with the Winkler, however, the water absorbed dilutes the whole of the acid, and the issuing air is saturated up to the vapour pressure of the solution.

(4) As by far the greater quantity of water is taken up in the inlet branch, it is only necessary to renew the acid in this branch for the vessel to be again efficient.

(5) For any prolonged run it is easily seen that less acid is required in the new form than in the Winkler.

In view of Mr. Manley's observations that sulphuric acid itself has an appreciable vapour pressure *, being, for example, found condensed on the lids of desiccators, experiments were made to ascertain the magnitude of any error that might be introduced by neglecting this effect.

Air at the laboratory temperature was passed over sulphuric acid in a vessel very similar to that already described and then over water. At the end of six days the water was tested with a drop of barium chloride solution, which, after standing some few minutes, gave a slight turbidity. By comparison with the turbidity produced by known amounts of sulphuric acid, the water was estimated to have contained ·0001 gramme of acid. The same experiment was repeated with the train of vessels immersed in a bath at 30° C., the air being passed for three days; again the amount of acid carried over into the water was found to be about ·0001 gramme.

It may be mentioned that during the operation of weighing, air, dried by passing over sulphuric acid, is circulated through the balance-case. So far there are no signs of any harm having been done to the balance. But an alternative method for drying the air seems to be to pass it over stick potash, as the following experiment shows :—

Air derived from outside the laboratory, during very

* *Loc. cit.*

rainy weather, was passed for 102 hours through a soda-lime tube * (1·5 metres long), the last third of which was filled with small pieces of potash, and then over a weighed sulphuric-acid vessel, with the result that the latter gained ·0041 gramme.

In this connexion it may be of interest to note that quantitative measurements show *pure* anhydrous $CuSO_4$ to be a very efficient drying agent for air containing little more than traces of moisture (it will take up about 0·05 per cent. of its own weight). It has the advantage that it can be used over again after heating to 210°–220° C. in an air-stream. The dehydrating property of $CuSO_4$ seems difficult of explanation, for, according to theory †, the substance should not absorb water-vapour unless the partial pressure is greater than that of the hydrate $CuSO_4 \, 1 \, Aq$.

LXII. *Note on a Sensitive Method for Examining some Optical Qualities of Glass Plates. By the* Earl of BERKELEY, *F.R.S., and* D. E. THOMAS, *M.A., B.Sc.*‡

IN the course of a research on the relation between the concentration and the partial pressures of the vapours of miscible liquids, we have used a Rayleigh interferometer for determining the refractive index of the vapours and their mixtures. The new method for the examination of glass plates arose out of certain troubles experienced in the adjustments of this instrument.

The interferometer is one of Zeiss's, designed for working with columns of gas one metre in length, and was modified so as to double the optical path as shown in figs. 1 and 2.

Fig. 1 is a plan of the apparatus as set up for the examination of glass plate X—the arrangement differs from that used in examining gases only in the removal of the

* These soda-lime tubes have proved to be very convenient; they are made in the shape of a very broad S (as seen in plan), the bends of the S are turned up at an angle of 45° with the horizontal and are fitted with ground-in glass stoppers for rapidity in filling. The vertical inlet and exit tubes are relatively narrow and carry mercury cups, and the whole tube can stand on the bench without supports.

† Cp. Lehfeldt's translation of van't Hoff's Lectures on Theoretical and Physical Chemistry, Part I. p. 60.

‡ Communicated by the Authors.

gas-tubes ; the Vincent mercury lamp *, M, gives a narrow
vertical source of light, which is focussed on the slit, S, of
the collimator, C. On the collimator, which contains Wratten
filters for isolating the green line, is fixed a metal plate, P,
cut so as to have two vertical slits, each 4 mm. wide, with their
inner edges 8 mm. apart. Light emerges from the colli-
mator in two parallel beams, which, striking a half silvered

Fig. 1.
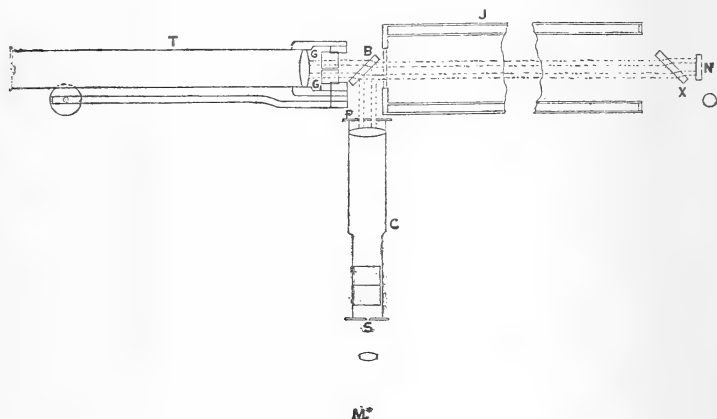
mirror, B, are reflected through the jacket, J, to a mirror, N,
fully silvered on its front surface. The reflected beams are
then brought to a focus by the objective of the telescope, T,
a lens of 30 cm. focal length. The interference pattern thus
produced is viewed by means of a cylindrical lens of very
short focal length.

Fig. 2.
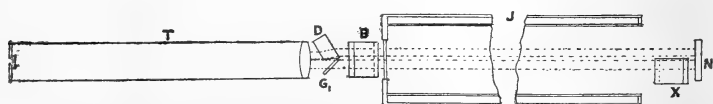
Fig. 2 gives an elevation of the apparatus, omitting the
collimator.

* This lamp was given to us by the Silica Syndicate Co., to whom
our thanks are due. The lamp is in the form of a capillary U tube (bore
about 1 mm.) made of fused silica—the light is generated in the capillary
by heating the mercury there until vapour is formed, it will then run
for hours on a direct current (100 volts) of 0·09 amp. Being very small
and compact (one form, giving a horizontal source of light, could be
carried in a waistcoat pocket), it can be placed exactly where wanted.

The upper part of the two beams, just before entering the telescope, is displaced downwards by the glass plate, B, with the result that, if the latter is properly adjusted, there will appear in the field of view a sharp horizontal line separating the upper and lower interference bands.

The lower part of the beams passes through the two thin glass plates, G and G_1; the former is fixed, and the latter is capable of rotating about a horizontal axis through its upper edge. The rotation of G_1, actuated by a long lever and micrometer screw, causes a change in the optical path of the lower right-hand beam and thus produces a bodily shift of the lower set of bands; the upper bands, as in Lord Rayleigh's original instrument, are merely a set of reference marks.

Testing the Plate.

The plate is placed at 45° to the optic axis as shown in the diagram (this we will call position " *a* "), with its upper edge as near as can be to the horizontal separating line. The upper and lower bands are now brought into coincidence and the reading of the micrometer head noted; at the same time the path of the two beams through the plate is located. The plate is now rotated through 180° (position " *b* "), and placed so that the light still passes through the same parts of the glass, the bands are again brought into coincidence and the reading noted; the difference between the readings is a measure of the difference in the optical paths in the two positions.

The optical arrangements were such that the central bright area of the interference pattern was traversed by four sharp black bands, and settings were always made on a certain one band. After a little practice it was found that the error of setting for either observer did not exceed half a scale-division from the mean of a number of settings. Since 50 scale-divisions correspond to one band interval, the shift of the lower band system can be measured to the 1/100 of a band; this corresponds to a retardation of one beam on the other of the 1/100 of the wave-length of the light used.

The following are a set of readings made in this manner :—

Observer.	Position of plate.	Readings.			Means.	Diff.
B	*a*	188·0	188·0	187·8	187·9	
B	*b*	192·0	192·0	192·2	192·1	4·2
T	*a*	187·0	187·0	186·5	186·8	
T	*b*	191·1	191·1	191·1	191·1	4·3

Other measurements made at different times and on slightly different parts of the plate confirmed these results.

If we assume, as an approximation, that placing the plate at an angle of 45° increases the relative retardation in the two beams by about 13 per cent., we get for the plate at right angles to the optic axis a retardation $(4\cdot25-\cdot55)/50 = \cdot074$ of a band. Hence, for a single transmission, the difference in paths $D(\mu-1) = \cdot037\,\lambda$.

Obviously this difference may lie in a variation in D or $\mu - 1$ or in both, and we are unable to distinguish; but we would draw attention to the fact that the condition for a perfect echelon spectroscope plate is precisely that $D(\mu-1) =$ constant, while Michelson's method [*], which is generally used for testing the figuring of these plates, only gives information on the product $D\mu$; over and above this, the method here described is some 30 per cent. more sensitive.

As regards sensitiveness, it is most probable that if the cylindrical lens were fitted at its focus with a fine vertical fibre just wide enough not to cover completely the bright space between the black bands in the upper field of view, then the lower bands could be fitted to the upper with extraordinary accuracy—this arrangement is the analogue of that used by Dr. C. V. Burton [†] in his micro-azimometer, where single settings were made with a probable error of 1/800 part of the width of the central bright band of a diffraction pattern.

The Practical Application of the Method.

Echelon plates are usually obtained by cutting up a large plate, which has been figured under the Michelson test, into strips, and these are then cut into the requisite lengths. It is obvious that, short of building a very large Rayleigh interferometer, the initial plate cannot be placed in our instrument. We would suggest, however, that if the above-mentioned strips were made somewhat wider than necessary they could be examined separately by our method and then refigured.

There are two ways by which such an examination may be made; both involve a comparison with a standard plate.

(1) By fitting the interferometer with a system of mirrors or prisms so as to separate the two beams widely enough (as outlined in fig. 3), we can get an " optical contour " of the strip by the direct comparison of its different parts with the standard.

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[*] Astrophysical Journal, vol. viii. 1898, p. 37.
[†] Phil. Mag. vol. xxiii. 1912, p. 385.

(2) Using the instrument as it is * (or better with a rather larger collimator and telescope and shorter air-path), the different parts of the strip may be compared with one another and finally with the ends, whose "optical thickness" can be separately referred to the standard.

Unfortunately, the first method, which is the more efficient, involves somewhat elaborate and substantial fittings for adjusting and fixing the mirrors.

Should it be found essential to figure the whole plate before cutting it up, the great advantage of the present instrument in having reference bands which are part of the same optical system as those under examination will have to be sacrificed. Burton's signal, mentioned above, placed on a travelling micrometer might be used, or another set

Fig. 3.

STANDARD PLATE

C

A

B

PLATE UNDER TEST
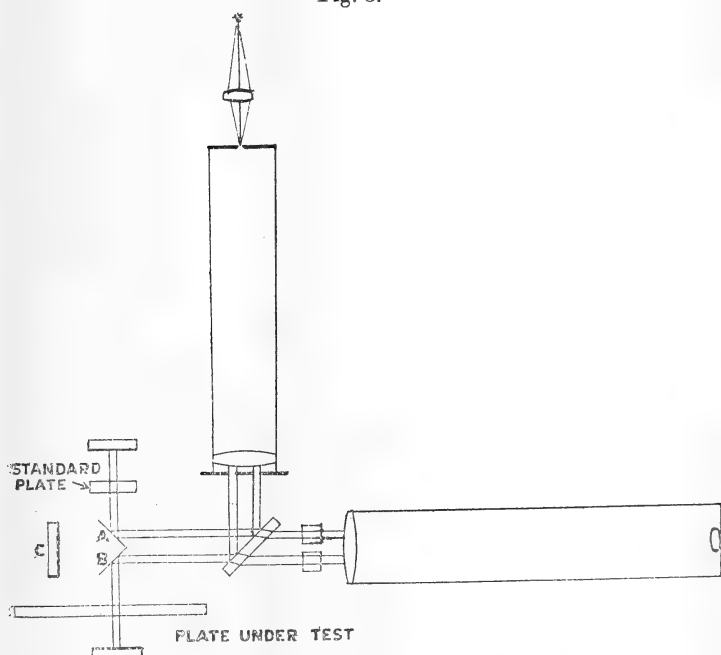
of reference bands could be obtained by modifying the arrangement shown in fig. 3, so that part of the two beams pass clear of the mirrors A and B to be reflected into the telescope by mirror C.

* A geometric fitting for ensuring that the standard plate and strips always have the same orientation would have to be provided.

LXIII. *The Photoelectric Effect*—III.   *By* O. W. Richard-
son, *F.R.S., Wheatstone Professor of Physics, University
of London, King's College, and* F. J. Rogers, *Associate
Professor of Physics, Stanford University, California* *.

IN the Philosophical Magazine, vol. xxvi. p. 549 (1913),
Dr. K. T. Compton and one of us published data for the
metals platinum, aluminium, sodium, and cæsium, showing
the relative photoelectric efficiency when a given amount of
energy fell upon them in the form of light of different wave-
lengths.   It was intended to reduce the measurements to
absolute values, but this was not possible at the time owing
to the absence of a suitable radiation standard.   This de-
ficiency has since been remedied and the results of the
measurements are given below.   They are to be taken in
conjunction with the numerical data and curves published
in the paper already referred to.

To reduce the current measurements to absolute values,
the only new data required were the capacities of the electro-
meter and the variable condenser which was added to the
quadrants in some of the experiments.   The capacity of the
electrometer and its connexions was found to depend to a
considerable extent upon the voltage on the needle.   This
was therefore determined separately for each of the different
voltages which had been used.   Both the method of mixtures
and a leakage method were employed, and the values obtained
when plotted against the potential of the needle were found
to increase regularly with the applied potential.   The new
values also agreed with the values in terms of the variable
capacity which had been used in reducing the measurements
described in the former paper, showing that the capacity of
the electrometer with a given potential on the needle had not
changed in the interval.

In the energy calibration in the former paper, the mono-
chromatic light from the illuminator was allowed to fall on a
linear thermopile provided with a slit adjusted to the same effec-
tive width as the strip used in the photoelectric measurements.
The steady thermo-electromotive force developed under the
influence of this radiation was balanced against the drop of
potential produced by the flow of a known small current
through a known small resistance.   In order to reduce the
former observations to absolute values, it was therefore
necessary only to determine the electromotive force gene-
rated in the thermopile when a beam of radiation of known
energy density was allowed to fall on it through the same
slit.   The source of radiation of known energy density was
a standard incandescent-lamp obtained from the Bureau of

* Communicated by the Authors.

Standards. This was set up at such a distance from the thermopile as to give rise to an electromotive force convenient to measure and comparable with those obtained with the monochromatic illuminator. The directions supplied with the standard were carefully followed. As a result of these measurements it was found that the unit of energy per unit time previously employed was equal to 0·404 erg per sec. For example, to reduce the values of E in Table IV, column 6, p. 562, to ergs per second, it is necessary to multiply each number by 0·404.

At this time the illuminator was readjusted and the energy distribution in the quartz-mercury arc-lamp spectrum redetermined. The values obtained were not sufficiently different from those given in the table just referred to, to call for comment.

We can now consider the results for each of the elements separately. The value of N, the quantity of electricity liberated when unit quantity of radiant energy falls on the metal, will be expressed in terms of the unit 1 coulomb per calorie. To reduce the numbers given to electrostatic units of quantity per erg, it is only necessary to multiply them by 72. The quantity N may also be appropriately termed the photoelectric yield, although it would be better to restrict the term photoelectric yield to the case in which the light is completely absorbed. The value of the photoelectric yield, in this sense, can be obtained from the data given, together with a knowledge of the reflecting power, in the different parts of the spectrum, of the metals concerned.

Platinum (loc. cit. p. 561).

Unit of $N = 9·05 \times 10^{-7}$ coul./cal.

Greatest value of N (at $\nu = 1·5 \times 10^{15}$ sec.$^{-1}$)

$= 3·0 \times 10^{-5}$ coul./cal.

Aluminium (loc. cit. p. 562).

Unit of $N = 1·91 \times 10^{-6}$ coul./cal.
for curves 1, 3, and 4.

Curve 1 (taken immediately after scraping the aluminium and setting up).

Maximum value of N (at $\nu = 1·36 \times 10^{15}$ sec.$^{-1}$)

$= 2·25 \times 10^{-4}$ coul./cal.

Curve 3 (72 hours later).

Maximum value of N (at $1·42 \times 10^{15}$ sec.$^{-1}$)

$= 1·01 \times 10^{-4}$ coul./cal.

Curve 4. This was for a flat strip at perpendicular incidence and was taken about 6 hours after scraping and setting up.

Maximum value of N (at $1·38 \times 10^{15}$ sec.$^{-1}$)

$= 1·28 \times 10^{-4}$ coul./cal.

Curve 5. This was taken somewhat later than curve 4, with the same flat strip set so that the light was incident at approximately 15°. Owing to the inclination of the strip the effective width of the beam of radiation falling on it was less than in the previous cases. Allowing for this, the unit of N is 1.98×10^{-6} coul./cal. and the maximum value of N (at $\nu = 1.37 \times 10^{15}$ sec.$^{-1}$)

$$= 9.7 \times 10^{-5} \text{ coul./cal.}$$

Sodium (loc. cit. p. 563).

Curve 1. The observations used in constructing this curve were commenced about one hour after distilling the sodium on to the strip and took over an hour to complete. There was a rapid photoelectric fatigue. This was corrected for by extrapolation ; so that all the observations were reduced to the values corresponding to the instant of the first observation. This extrapolation cannot be made quite exact since different parts of the curve decay at different rates. This difference was allowed for in so far as it could be ascertained ; so that Curve 1 may be taken as representing the emission from a surface of distilled sodium one hour after distillation. The unit of N for this curve is 2.56×10^{-5} coul./cal.

Curve 2. This curve represents the actual condition of affairs $2\frac{1}{2}$ hours after distillation. There is some doubt, arising from a possible inaccuracy in one of the data used in correcting for fatigue, about the position of the curve for values of $\nu \times 10^{-13}$ greater than 125. Relative to the rest of the curve on the left-hand part of the diagram, the point at $\nu \times 10^{-13} = 125$ is correct ; but the true position of the maximum at $\nu \times 10^{-13} = 133$ may be 10 per cent. below the value on the curve as drawn, and the end point at $\nu \times 10^{-13} = 150$ as much as 30 per cent. below the value shown, intermediate points dropping by regularly increasing percentages. The unit of N for this curve is 1.31×10^{-5} coul./cal.

Curve 3. This represents the state of affairs 18 hours after preparation, when the rate of fatigue was extremely slow. The unit of N for this curve is 6.25×10^{-6} coul./cal.

The values of the quantity of electricity emitted per unit energy of incident (isotropic) radiation are collected in the following table. The values at $t = 0$ have been derived on the assumption that the decay of the photoelectric effect is exponential for the first $2\frac{1}{2}$ hours. As there is a certain amount of experimental evidence indicating that under certain circumstances, not yet properly understood, the emission may show an initial increase followed by decay according to an exponential law—as well as other types of behaviour under different conditions—these numbers may be

altogether wrong. For this reason, and as they are extra-polations and not actually observed values, they are enclosed in square brackets.

Sodium.

Time from preparation of surface.	Value of **N** for First Maximum (*a*).	Value of N for Second Maximum (*b*).
[0] hours.	$[47 \times 10^{-4}]$ coul./cal.	$[33 \times 10^{-4}]$ coul./cal.
1 ,,	$17 \cdot 1 \times 10^{-4}$,,	$19 \cdot 7 \times 10^{-4}$,,
2·5 ,,	$3 \cdot 6 \times 10^{-4}$,,	8×10^{-4} * ,,
18 ,,	$0 \cdot 59 \times 10^{-4}$,,	$2 \cdot 44 \times 10^{-4}$,,

Cæsium (loc. cit. p. 564).

Owing to an oversight the capacity used in the original measurements with this substance has not been recorded, and as we had not time to repeat the measurements before leaving Princeton, the data we are able to furnish have only a qualitative significance. It appears from the possible values of the capacity, and the other data, that the value of N for the maximum point on the curve at $\nu = 1 \cdot 2 \times 10^{15}$ sec.$^{-1}$ must lie between the limits :—

$$1 \times 10^{-5} \text{ and } 5 \times 10^{-5} \text{ coul./cal.}$$

The value of the unit of N varies of course between corresponding limits.

These numbers, although very wide apart, are of consider-able interest. They show that cæsium under the conditions of the experiments previously described is very inefficient photoelectrically. It is very much worse than sodium, con-siderably worse than aluminium, and comparable with platinum in this respect. In view of the highly electro-positive character of cæsium, this result seems very surprising and rather points to the view that the cæsium used in these experiments was already much fatigued before the observations commenced. This position is supported by the following additional considerations :—

(1) The absence of fatiguing during the observations which was remarked in the previous paper.

(2) The absence of the expected first hump, which, if the experiments with sodium may be taken as a guide, dies out more quickly than the second.

(3) If, as seems to be the case in general, photoelectric fatigue is more rapid the more electropositive the metal, we should expect it to be accomplished more quickly with cæsium than with sodium; so that it well might be practi-cally complete before the actual observations commenced.

In our opinion it is desirable to examine the photoelectric

* This number may be 10 per cent. too high (see above).

spectrum of cæsium under better conditions from the standpoint of preventing fatigue.

Previous measurements of absolute photoelectric efficiency have been made by S. Werner [*] with sputtered films of gold, platinum, silver, bismuth, and copper, and by Pohl and Pringsheim [†] with surfaces of calcium, sodium, potassium and potassium amalgams of different concentrations. For a platinum film deposited in hydrogen at 0·6 mm. pressure, Werner finds at $\nu = 1\cdot36 \times 10^{-15}$ that 1 calorie of radiation liberates $5\cdot6 \times 10^{-4}$ coulomb. The value for platinum at this frequency found in the present paper is 2×10^{-5} coulomb per calorie. Werner's value is for complete absorption of the radiation, whereas our value is reckoned per unit incident energy of (isotropic) radiation.

Werner also made some rough measurements of the emission from surfaces of ordinary (not sputtered) platinum, and it appears from the data given by him that the value for complete absorption by the hydrogen sputtered film requires to be reduced by the following factors to obtain the value for radiation incident on a surface of ordinary platinum, viz. :—

$\frac{1}{2}$ on account of the reflected light;

$\frac{2}{5}$ on account of the observed greater sensitiveness of hydrogen films compared with films sputtered in nitrogen ; and

$\frac{1}{20}$ on account of the greater sensitiveness of the nitrogen films compared with surfaces of polished platinum.

According to these figures the total reduction factor is $\frac{1}{2} \times \frac{2}{5} \times \frac{1}{20} = \frac{1}{100}$; so that under the conditions of our experiments Werner's numbers would give a sensitiveness at $\nu = 1\cdot36 \times 10^{15}$ sec.$^{-1}$ of about $5\cdot6 \times 10^{-6}$ coul./cal. This is only just over one-fourth of the value given by our measurements.

The values for sodium one hour after distillation are practically the same as those found by Pohl and Pringsheim $(17 \times 10^{-4}$ as compared with $15-19 \times 10^{-4}$ coul./cal.) so far as the first maximum is concerned. For values of $\nu > 10^{-15}$ sec.$^{-1}$ the curve does not agree with their typical curves but is more like that given by the figures in the last column of Table I. of their paper (loc. cit. p. 176). According

[*] *Ark. f. Math., Fys. o. Astr.* Bd. viii. Nr. 27, Upsala (1912), Diss. Upsala (1913).

[†] *Verh. der Deutsch. Physik. Ges.* xv. Jahrgang, p. 111, p. 173, p. 431 (1913).

to the observations of Compton and Richardson, the relative magnitude of the two humps is determined by the amount of photoelectric fatigue which has occurred. The data of both pairs of observers can be harmonized on the following assumptions :—

(1) That Pohl and Pringsheim's typical curves correspond to a state of less advanced photoelectric fatigue. This involves the assumption of the attainment of better vacuum conditions in their experiments, which seems to be borne out by an examination of the general character of their results.

(2) That the first hump (the "resonance" hump (a)) is present from the beginning, or at least is formed very quickly, and does not suffer much alteration in the earlier stages of the photoelectric fatigue.

(3) That the second hump is small initially, and increases to a maximum value during the early stages of fatigue. According to Compton and Richardson's experiments, this initial increase is followed by a decay, which is slower than that of the first hump, as the fatigue progresses.

It is not claimed that this is the only possible explanation of the observed differences; it is put forward as a possible, and, on the whole, rather probable one.

LXIV. *The Contact Difference of Potential of Distilled Metals. By* Fernando Sanford[*].

I T has seemed to the present writer that some of the results of the experiments published under the above caption in the September number of this Journal, may perhaps be accounted for in a manner not taken into consideration by Mr. Hughes. I refer especially to the observation that after a film of zinc or bismuth had been condensed from the metallic vapour upon a very thin film of platinum on a glass plate in a high vacuum, the condensed metallic film was at first much less electropositive to the platinum film than it became after standing for some time, and that the change to the more electropositive condition was hastened by admitting a very small quantity of air to the vacuum.

In some experiments which I have made for another purpose I have observed that when a section of a glass tube is heated to a temperature of 100 degrees, or even less, it becomes plainly electronegative to the colder parts of the same tube. The change is necessarily slow, since, on account of the low conductivity of glass, the electrons require considerable time to gather in the heated parts of the glass. It would seem that

in Mr. Hughes' experiments the glass must have been considerably heated over the regions upon which the metallic films were condensed. If this heating process was kept up for some time the glass in these regions probably became negatively electrified, and accordingly lessened the electropositive inductive effect of the metallic films upon the plate connected to the electrometer. As the glass cooled off, its charge diffused slowly and the metallic films appeared to become more electropositive. The admission of a small amount of air, by lowering the insulation of the high vacuum, would then enable the negative charge on the glass to diffuse more rapidly.

Stanford University, Cal.
Dec. 26, 1914.

LXV. *Notices respecting New Books.*
Bulletin of the Bureau of Standards. Vol. X. (1914).
Washington : Government Printing Office.

THIS volume of the Bulletin (Nos. 1, 2, 3 and 4) exhibits the great activity of the Bureau. It contains amongst other papers the following :—(i.) Constants of Spectral Radiation of a uniformly heated enclosure, by W. W. Coblentz, in which are described experiments with enclosures with white and with black walls, which yield as mean values of Planck's constants : $C = 14456 \pm 4$ micron deg.; $A = 2911$ micron deg. (results of 94 energy curves). (ii.) Melting-points of the refractory elements of atomic weight from 48 to 59, by G. K. Burgess and R. G. Waltenberg. The summary results for the probable melting-points of the pure elements are : nickel $1452 + 3$, cobalt 1478 ± 5, iron $1530 + 5$, manganese 1260 ± 20, chromium 1520 to $>$ iron ?, vanadium 1720 ± 30, titanium 1795 ± 15. (iii.) Latent heat of fusion of ice, by H. N. Dickinson, D. R. Harper, and N. S. Osborne. Final result (mean of 21 determinations) $79 \cdot 63$ cal$_{15}$ per gram. Mean of experiments by electrical method $79 \cdot 65$, by method of mixtures $79 \cdot 61 \pm \cdot 02$; electrical method (second set, ice at $- 3° \cdot 78$), $79 \cdot 65$. (iv.) Melting-points of some refractory oxides, by C. W. Kanolt. (v.) The pentane lamp as a working standard, by E. C. Crittenden and A. H. Taylor. (vi.) Comparison of the silver and iodine voltameters and the determination of the Faraday, by G. W. Vinal and St. J. Bates. Results : E. Ch. Eq. of iodine $1 \cdot 31502$; value of Faraday (iodine=$126 \cdot 92$) 96515; (Ag=$107 \cdot 88$) 96494. Recommended value for general use, 96500. (vii.) Production of temperature uniformity in an electric furnace, by A. W. Gray. (viii.) The silver voltameter, by E. B. Rosa, G. W. Vinal, and A. S. McDaniel. (ix.) Flame standards in Photometry, by E. B. Rosa and E. C. Crittenden.

The Bureau publishes these papers in separate form ; also a set of technological papers. Amongst its recent circulars are one on the testing of barometers and a valuable one on Polarimetry (*i. e.* of sugars). It has also just published a decennial index to the Bulletin (Vols. 1–10).

Fig. 34.

Fig. 36.

Fig. 40.

Fig. 42.

Fig. 46.

Fig. 48.

Fig. 52.

Fig. 54.

VINCENT & JUDE

Phil. Mag. Ser. 5 Vol. 23 P. VIII
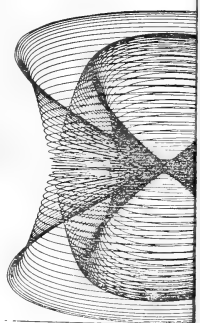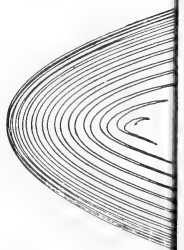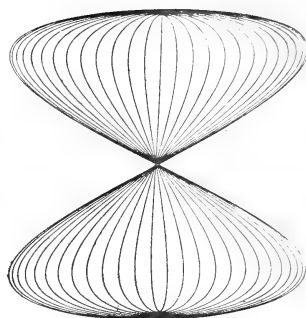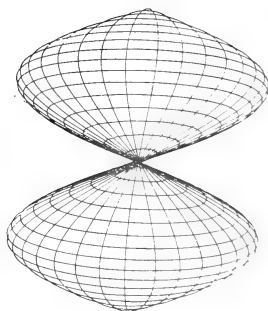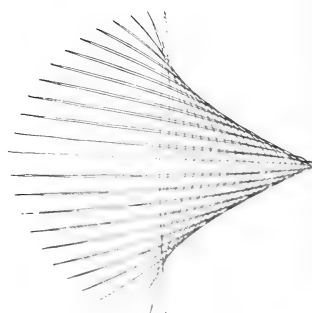
FIG. 1.   FIG. 2.   FIG. 3.   FIG. 4.   FIG. 5.   FIG. 6.

FIG. 7.   FIG. 8.   FIG. 9.   FIG. 10.   FIG. 11.   FIG. 12.
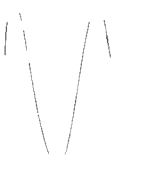
FIG. 13.   FIG. 14.   FIG. 15.   FIG. 16.   FIG. 17.   FIG. 18.
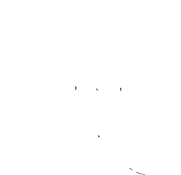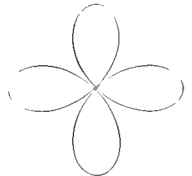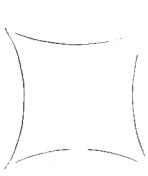
FIG. 19.   FIG. 20.   FIG. 21.   FIG. 22.   FIG. 23.   FIG. 24.
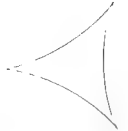
FIG. 25.   FIG. 26.   FIG. 27.   FIG. 28.   FIG. 29.   FIG. 30.
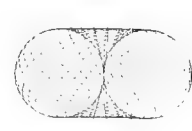
FIG. 31.   FIG. 32.   FIG. 33.   FIG. 34.   FIG. 35.   FIG. 36.
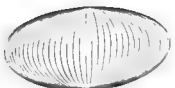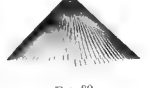
FIG. 37.   FIG. 38.   FIG. 39.   FIG. 40.   FIG. 41.   FIG. 42.
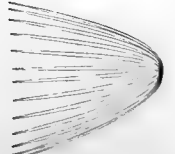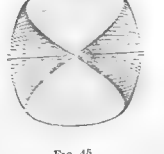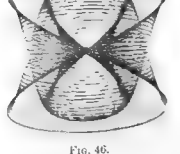
FIG. 43.   FIG. 44.   FIG. 45.   FIG. 46.   FIG. 47.   FIG. 48.
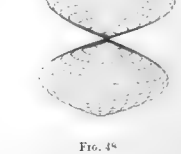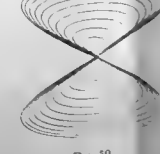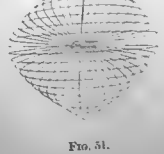
FIG. 49.   FIG. 50.   FIG. 51.   FIG. 52.   FIG. 53.   FIG. 54.

A.

B.

C.

D.

E.

G.

F.

H.

KING.

Phil. Mag. Ser. 6, Vol. 29, Pl. X.
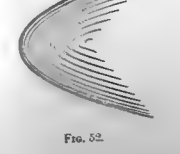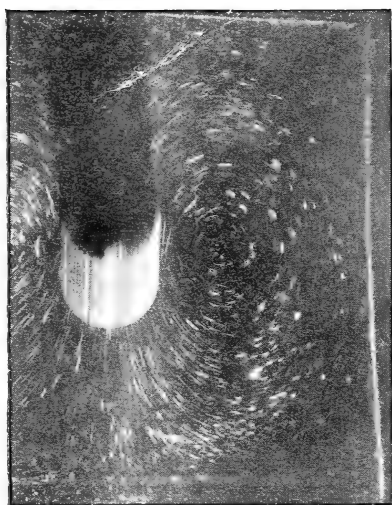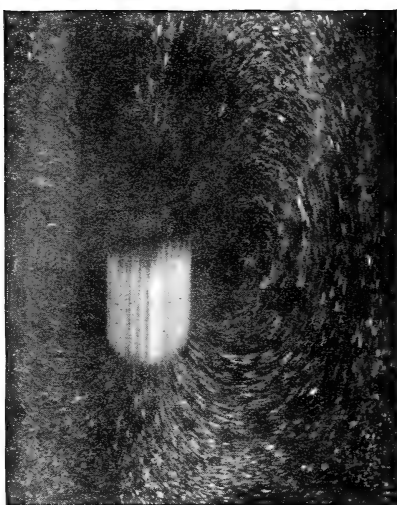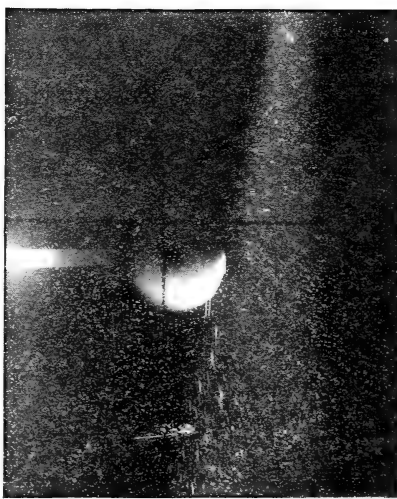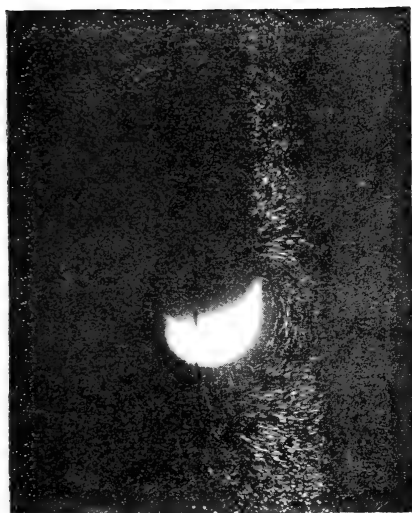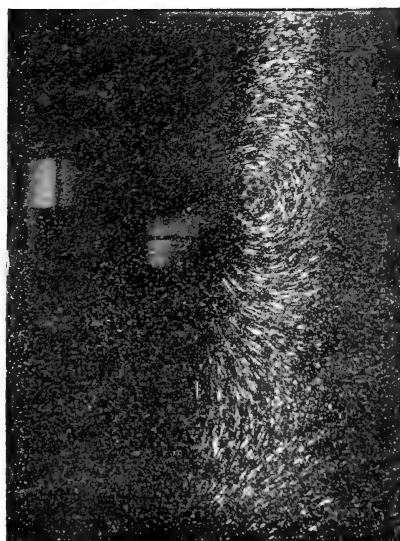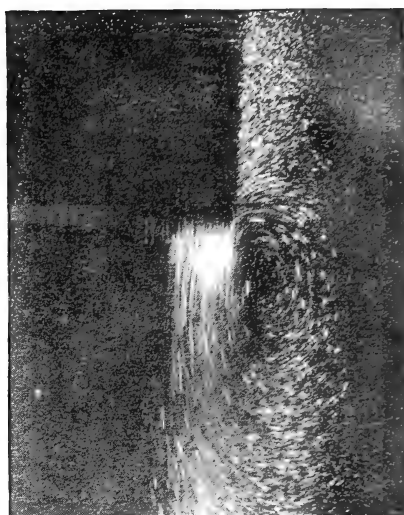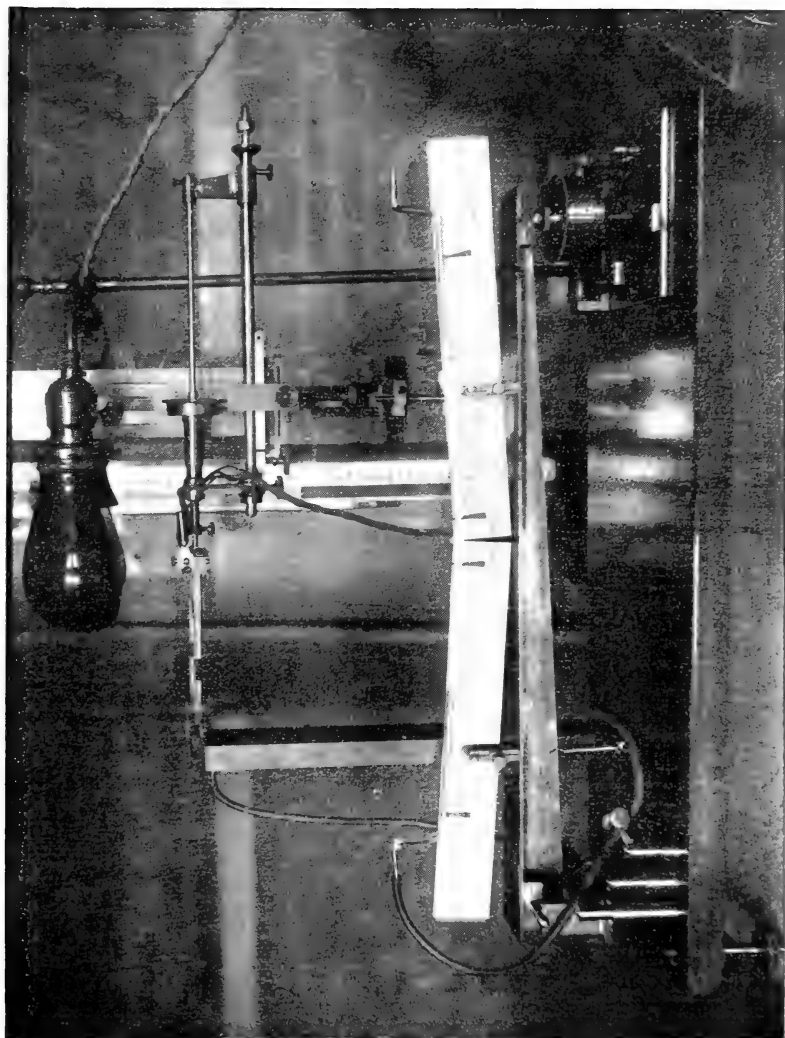
Linear Hot-Wire Anemometer,

showing micrometer mounting. Lower part of figure shows a
Töpler manometer for measuring minute pressure differences.

LXVI. *The Scattering and Regular Reflexion of Light by Gas Molecules.*—Part I. *By* C. V. BURTON, *D.Sc.*[*]

1. I HAVE been so much interested in reading a memoir by Lord Rayleigh[†] in the February number of the Phil. Mag., that time has had to be found for the completion of this paper, which had been laid aside since last August. The "simple aërial resonator vibrating symmetrically" is undoubtedly more mathematically tractable than a radiating molecule; and in this paper also, problems relating to such resonators (or, more generally, secondary vibrators) are considered by way of introduction. But, as will appear in Part II., the difficulties arising from our ignorance of the mechanism [‡] of radiation can for the most part be evaded. Something has, indeed, to be assumed as to the influence of the orientation of the molecule on its response to incident radiation, and, by way of illustration, two alternative assumptions have been made, representing perhaps the extremes of possibility. Much of the analysis—for example, that which deals with reflexion from a three-dimensional multitude of vibrators—is equally applicable to the acoustical and to the optical case: whichever case is in question, there

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[*] Communicated by the Author.
[†] "Some Problems concerning the Mutual Influence of Resonators exposed to Primary Plane Waves," Phil. Mag. Feb. 1915, pp. 209–222.
[‡] If, indeed, mechanism is not a wholly improper term in this connexion.

is an essentially similar transition from diffuse to regular reflexion as the distribution of the vibrators becomes denser.

2. The present investigations deal exclusively with vibrators which scatter, without absorbing, wave-energy of definite frequency, though their extension to molecules which absorb some part of the incident energy should present no difficulty. Wood [*] has lately emphasized the importance of determining experimentally to which category the resonant atoms of mercury vapour belong, and in the second part of this paper some tentative suggestions are made towards that end.

3. The case of an isolated " simple aërial resonator, excited by plane waves," has been dealt with by Rayleigh in the paper already cited ; and the result (with a changed notation) may be stated as follows.   Let the primary waves be defined by the velocity-potential

$$\psi = \mathrm{A} \cos (pt - vx), \quad \ldots \ldots (1)$$

where $p/2\pi$ is the frequency and $2\pi/v$ the wave-length ; then the secondary disturbance due to a resonator at the origin is

$$\psi' = \frac{\mathrm{C}}{r} \cos (pt - vr - \gamma), \quad \ldots \ldots (2)$$

where γ is the lag in phase and

$$\mathrm{C} = \frac{\mathrm{A}}{v} \sin \gamma. \quad \ldots \ldots (3)$$

This last relation is deduced from the sole assumption that the resonator merely *scatters* sonorous energy without changing its total amount.

4. Consider next a square, forming part of the plane of yz and having for its sides $y = \mp \frac{1}{2}b$, $x = \mp \frac{1}{2}b$.   Let simple Helmholtz vibrators be distributed over the surface of this square *with complete irregularity like the molecules of a gas,* the average number of vibrators per unit of area being σ. For the moment, the only restriction made regarding σ is that the aggregate surface occupied by the vibrators is insignificant in comparison with the spaces between them. It is simply postulated that all the vibrators are sending out vibrations of the same amplitude and phase, represented typically for the nth vibrator by

$$\psi_n = \frac{\mathrm{C}}{r_n} \cos (pt - vr_n). \quad \ldots \ldots (4)$$

The manner in which the vibrators are kept going is not the

immediate object of inquiry ; what has to be determined is the relation between the energy of the plane waves propagated in the direction (say) of x decreasing and the energy diffusely scattered. To find the plane-wave energy, imagine a sufficiently large (acoustical) lens of focal length f placed in front of the square $b \times b$; an "image" will be formed at the principal focus, and will take the form of a diffraction pattern whose scale is determined by $f\lambda/b$; λ being the wave-length concerned, and equal to $2\pi/v$. It will be convenient to suppose f so large that the lens, having degenerated into a sensibly flat plate, may be removed, and so need trouble us no further.

5. No matter how sparsely the vibrators are spread in the yz-plane, we can postpone the discussion of more delicate points by taking the square $b \times b$ so large that it can be divided up into numerous elements, each containing many vibrators ; f will then, perhaps, be enormous, but that does not matter : we can apply the methods familiar in physical optics to determine the distribution of disturbance in the diffraction pattern. In any case it conduces to simplicity that $b : \lambda$ should be large. In the plane $x = -f$, taking y', z' as current coordinates, $y' = 0$, $z' = 0$ is the position of the geometrical "image," and at that point the amplitude * due to σb^2 vibrators, all acting in complete agreement of phase, is $\sigma b^2 a$; where a is the amplitude due to a single vibrator at distance f. The distribution of amplitude (g) over the diffraction pattern is thus known to be

$$g = \sigma b^2 a \frac{\sin \alpha}{\alpha} \frac{\sin \beta}{\beta},$$

where $\alpha = \pi b x'/\lambda f$, $\beta = \pi b y'/\lambda f$.

6. As an arbitrary measure of the energy of the "image" we may take the surface-integral of g^2 over the diffraction pattern; that is, in effect (since $dx' = \lambda f d\alpha/\pi b$, $dy' = \lambda f d\beta/\pi b$),

$$\frac{\sigma^2 b^2 a^2 \lambda^2 f^2}{\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\sin^2 \alpha}{\alpha} \frac{\sin^2 \beta}{\beta} d\alpha d\beta$$

$$= \frac{\sigma^2 b^2 a^2 \lambda^2 f^2}{\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\sin \alpha}{\alpha} \cdot \frac{\sin \beta}{\beta} d\alpha d\beta$$

$$= \sigma^2 b^2 a^2 \lambda^2 f^2.$$

7. The energy diffusely scattered has next to be considered. With the origin as centre let a sphere of radius f

---

* Amplitude of pressure-variation for example.

be described; the plane $x = -f$ touches this sphere, and over the small area effectively covered by the diffraction pattern the sphere and the plane are indistinguishable. Excluding from consideration that small area, and a like area at the opposite pole $(f, 0, 0)$, take some definite point P on the surface of the sphere. If, then, Q is any point within the square $b \times b$, the length PQ may lie anywhere between limits which differ by a large number of wave-lengths; and if a vibrator placed at Q is sending forth a disturbance (4) of prescribed phase, the phase in which this disturbance reaches P may be any whatever: under the conditions of the problem all phases are equally likely, *and this is true for each vibrator independently of the other vibrators.* Hence it follows that, on an average, the (amplitude)^2 at the point P is equal to a^2 (that due to a single vibrator) multiplied by σb^2 the number of vibrators *. The expression $\sigma b^2 a^2$, being constant over practically the whole spherical surface, has only to be multiplied by $4\pi f^2$ to furnish the total diffusely radiated energy, on the arbitrary scale already used. Thus, finally, the plane-wave energy, *reckoned in one direction only*, bears to the scattered energy the ratio

$$\sigma^2 b^2 a^2 \lambda^2 f^2 / 4\pi \sigma b^2 a^2 f^2 = \sigma \lambda^2 / 4\pi = \pi \sigma / v^2. \quad . \quad . \quad . \quad (5)$$

8. No matter how thinly the plane of yz is besprinkled with vibrators, this result is perfectly definite, provided only that we can deal with a sufficiently extended area to be able to assign a definite value to σ. We are led to the conclusion that the motion given out by the vibrators can be *sharply* divided into two categories: plane waves and irregular disturbance. If the vibrators are restricted to a finite area, the plane waves and the irregular disturbance become sorted out from one another at great distances, or at a more moderate distance with the help of a lens. Their energies are, of course, simply additive.

9. It is otherwise evident that a portion of the resultant disturbance from a plane distribution of synchronous vibrators must be assignable to plane waves of unique specification. For if the activity of the vibrators is due to the incidence of primary plane waves, these waves must pass on with diminished amplitude, and (in general) with altered phase; from a knowledge of which things the amplitude and phase of the secondary plane waves emitted by the vibrators could be written down. From considerations of symmetry we should then know likewise the amplitude and phase of the

* *Cf.* Rayleigh, "Wave Theory of Light," § 4. Encycl. Brit. vol. xxiv. (1888); Collected Papers, vol. iii. art. 148.

regularly reflected waves, and the ratio of their energy to that of the incident train. Now in a medium such as we consider, plane waves retain their simple character as we trace them back, even up to the plane of vibrators in which they originated. At points close to, or in, that plane, there will naturally be immense inequalities of disturbance, but *all these inequalities belong to the irregular motion*, and have nothing to do with the regular waves. A recognition of this fact leads to great simplification in the problems which here concern us : for example, a three-dimensional swarm of vibrators can be divided up into laminæ, each of which, in regard to normally incident plane waves, behaves in a very simple manner.

10. Suppose, now, that there is a completely irregular distribution of secondary vibrators over the plane of yz, the number per unit of area being σ ; and for the moment suppose σ to be small enough to justify the assumption that all the vibrators send out disturbances of the same amplitude and phase when excited by the primary waves (1). In § 24 it will be shown that this restriction can be removed.

11. Let the secondary disturbance due to the vibrators be

$$\psi' = \Sigma \frac{C}{r_n} \cos (pt - vr_n - \gamma) ; \quad . \quad . \quad . \quad (6)$$

then it is the plane waves comprised in (6) that have to be determined. In the diagram O is the origin, P a point $(x, 0, 0)$,
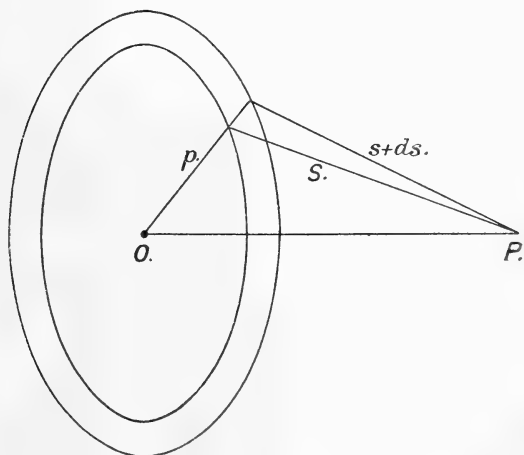
$\rho = \sqrt{(y^2 + z^2)}$ the distance from O to any point Q in the plane of yz, and $PQ = s$. As in the figure, draw two circles with O as centre and radii ρ, $\rho + d\rho$; the annulus between

them contains $2\pi\sigma\rho d\rho = 2\pi\sigma s ds$ secondary vibrators, whose contribution to the velocity potential of emitted plane waves is, for x positive,

$$d\psi'' = 2\pi\sigma \, s ds \, . \frac{C}{s} \cos(pt - vs - \gamma),$$

whence

$$\psi'' = -\frac{2\pi\sigma C}{v} \left| \sin(pt - vs - \gamma) \right|_{s=x}^{s=R}.$$

The upper limit is written as $s = R$ instead of $s = \infty$ for the sake of definiteness, the sheet of vibrators being limited to a circle of such great radius ρ_1 (say), that R or $\rho_1 \sqrt{(1 + x^2/\rho_1^2)}$ is as nearly as we please constant over those values of x with which we concern ourselves. Thus, within a constant,

$$\psi'' = -\frac{2\pi\sigma C}{v} \cos\left(pt - vx - \gamma + \frac{\pi}{2}\right). \quad . \quad . \quad (7)$$

12. In particular, if the vibrators are tuned to resound to the frequency of the primary waves, $\gamma = \frac{1}{2}\pi$ and

$$\psi'' = -\frac{2\pi\sigma C}{v} \cos(pt - vx). \quad . \quad . \quad . \quad (8)$$

For points in the yz-plane, the total *regular* disturbance is represented by

$$(\psi + \psi'')_{x=0} = (A - 2\pi\sigma C/v) \cos pt,$$

and for the amplitude-constant C of the disturbance emanating from each resonator, we have by § 3 (since the amplitude of the exciting waves is no longer A but $A - 2\pi\sigma C/v$),

$$C = A/v - 2\pi\sigma C/v^2,$$

that is

$$C = \frac{A}{v} \bigg/ \left(1 + \frac{2\pi\sigma}{v^2}\right);$$

so that finally

$$\left. \psi'' = -\frac{wA}{1+w} \cos(pt - vx) \right\} \quad . \quad . \quad . \quad . \quad (9)$$

where $w \equiv 2\pi\sigma/v^2$

Similarly for negative values of x, that is to say in the reflected wave,

$$\psi''' = -\frac{wA}{1+w} \cos(pt + vx). \quad . \quad . \quad . \quad (9\,a)$$

13. The energy per unit area of the primary waves ψ (arbitrarily represented by unity), diminished by the energy

of the transmitted waves $\psi + \psi''$ and of the reflected waves ψ''', gives for the energy diffusely scattered

$$1 - \left(1 - \frac{w}{1+w}\right)^2 - \left(\frac{w}{1+w}\right)^2 = 2w/(1+w)^2.$$

The energy of the reflected waves, referred to the same standard, is $w^2/(1+w)^2$; and the ratio of regularly reflected to scattered energy is $w/2 = \pi\sigma/v^2$, in agreement with (5).

14. The more general case where the vibrators are not tuned as resonators ($\gamma \neq \frac{1}{2}\pi$) need not be discussed at length, since its solution can be derived (§ 23) from that of a still more general problem. But it will be useful to write down the expressions for the secondary plane waves when $2\pi\sigma/v^2$ is negligible in comparison with unity. From (2), (3), and (7) these are readily seen to be

$$\psi'', \; \psi''' = -\frac{2\pi\sigma A \sin\gamma}{v^2} \cos\left(pt \mp vx - \gamma + \tfrac{1}{2}\pi\right)$$

corresponding to the primary waves (1).

15. It will now be convenient to introduce complex quantities. When, in place of (1), we write for the primary waves

$$\psi = A \exp i\,(pt - vx); \quad . \quad . \quad . \quad . \quad (10)$$

the plane waves emitted by σ secondary vibrators per unit of area in the plane of yz are

$$\psi'', \; \psi''' = -\frac{2\pi\sigma A \sin\gamma}{v^2} \exp i\{pt \mp vx - \gamma + \tfrac{1}{2}\pi\}$$

$$= -kA \exp i(pt \mp vx), \quad . \quad . \quad . \quad . \quad (11)$$

where
$$k = \frac{2\pi\sigma \sin\gamma}{v^2} \exp i(\tfrac{1}{2}\pi - \gamma). \quad . \quad . \quad (12)$$

16. Suppose, now, that in the space between the planes $x=0$ and $x=L$ there is a statistically homogeneous swarm of secondary vibrators, the average number of vibrators per unit of volume being ν. For the most part, no restriction is imposed on the value of ν, but when ν is small enough for the aggregate bulk of the vibrators in any considerable volume to be but an insignificant fraction of that volume— the vibrators being then distributed like the molecules of a gas—some of the results already obtained become applicable. Consider the lamina bounded by the planes x', $x' + dx'$: dx' being in any case very small compared with the wave-length of the primary disturbance (10) ; for the moment let it also be chosen so small that $2\pi\nu dx'/v^2$ is a negligible fraction.

This will enable us to make use of the formula (11), (12) provided *only* that the value of ν conforms to the restriction already indicated ; the vibrators in the lamina dx' being sensibly a plane distribution for which $\sigma = \nu dx'$. Writing $\chi dx'$ in place of k in (12) we have

$$\chi = \frac{2\pi\nu \sin\gamma}{v^2} \exp i\left(\tfrac{1}{2}\pi - \gamma\right) \left.\begin{array}{c} \\ \\ \end{array}\right\} \quad . \quad . \quad . \quad . \quad (13)$$

provided ν is not too great;

expressing, as to intensity and phase, the relation between the *resultant* plane waves incident on the lamina dx' and the plane waves emitted by the vibrators contained in that lamina.

17. But even if ν is too great to allow of a gas-like distribution of vibrators, so that (13) no longer holds good, the homogeneousness of the swarm of vibrators still leads to the conclusion that χ is a (complex) constant ; or, in other words, that the waves emitted by an elementary lamina dx' have an amplitude proportional jointly to dx' and to the amplitude of the resultant incident plane waves, with a phase differing from that of the incident waves by a constant.

18. Understanding, then, that ν is quite unrestricted, let the waves originally incident on the slab $0 < x < \mathrm{L}$ be represented by (10), and let the waves given out by the lamina x' to $x' + dx'$ be

$$\mathrm{B}'\exp i\{pt - v(x - x')\}dx', \quad \mathrm{B}'\exp i\{pt + v(x - x')\}dx', \quad . \quad (14)$$

where B' is a function of x', and is in general complex. At any plane $x = x''$, for which x'' lies within the limits 0, L the total disturbance arriving is

$$\mathrm{A}\exp i(pt - vx'') + \int_0^{x''} \mathrm{B}'\exp i\{pt - v(x'' - x')\}dx'$$

$$+ \int_{x''}^{\mathrm{L}} \mathrm{B}'\exp i\{pt + v(x'' - x')\}dx'$$

$$\equiv \mathrm{E}''\exp ipt, \text{ say}; \quad . \quad . \quad (15)$$

so that E'' is a complex function of x''.

19. Now by definition of χ the waves emitted by the lamina dx'' will be

$$-\chi \mathrm{E}''\exp i\{pt - v(x - x'')\}, \quad -\chi \mathrm{E}''\exp i\{pt + v(x - x'')\};$$

and these (on replacing single by double accents) must be identical with (14) ; that is

$$\chi^{-1}\mathrm{B}'' + \mathrm{E}'' = 0,$$

or

$$\chi^{-1}B'' + A \exp i(-vx'') + \int_0^{x''} B' \exp i\,v(-x''+x')dx'$$
$$+ \int_{x''}^L B' \exp i\,v(x''-x')dx' = 0.$$

The double accents being dropped, this may be written

$$\chi^{-1}B + A \exp(-i\xi) + v^{-1}\exp(-i\xi)\int_0^\xi B' \exp i\,\xi'd\xi'$$
$$+ v^{-1}\exp i\xi \int_\xi^\eta B' \exp(-i\xi')d\xi' = 0\,;\ (16)$$

where
$$\xi \equiv vx \equiv 2\pi x/\lambda, \quad \eta \equiv vL.\ \ .\ \ .\ \ (17)$$

20. To (16) add the equation obtained by differentiating (16) twice with respect to ξ. The definite integrals are eliminated, and we get

$$\frac{d^2B}{d\xi^2} = -\left(1 - \frac{2i\chi}{v}\right)B,$$

of which the solution is

$$B = C_1 \exp i\mu\xi + C_2 \exp(-i\mu\xi)\,;\ .\ \ .\ \ (18)$$

where
$$\mu \equiv \sqrt{(1 - 2i\chi/v)},\ .\ \ .\ \ .\ \ .\ \ (19)$$

and C_1, C_2 are constants, to be determined by substituting the expression found for B in (16). This now becomes

$$0 = \chi^{-1}\{C_1 \exp i\mu\xi + C_2 \exp(-i\mu\xi)\} + A \exp(-i\xi)$$
$$+ v^{-1}\exp(-i\xi)\int_0^\xi \{C_1 \exp i\mu\xi' + C_2 \exp(-i\mu\xi')\} \exp i\xi'd\xi'$$
$$+ v^{-1}\exp i\xi \int_\xi^\eta \{C_1 \exp i\mu\xi' + C_2 \exp(-i\mu\xi')\} \exp(-i\xi')d\xi'\,;\ (20)$$

which must hold good for all values of ξ from 0 to η. Thus, when $\xi = 0$

$$0 = A + \chi^{-1}(C_1 + C_2) + C_1 v^{-1}\left|\frac{\exp i(\mu-1)\xi'}{i(\mu-1)}\right|_{\xi'=0}^{\xi'=\eta}$$
$$+ C_2 v^{-1}\left|\frac{\exp\{-i(\mu+1)\xi'\}}{-i(\mu+1)}\right|_{\xi'=0}^{\xi'=\eta}$$

or

$$-A(\mu^2 - 1) = C_1\Big\{(\mu^2-1)\chi^{-1} - iv^{-1}(\mu+1)\exp i(\mu-1)\eta + iv^{-1}(\mu+1)\Big\}$$
$$+ C_2\Big\{(\mu^2-1)\chi^{-1} + iv^{-1}(\mu-1)\exp\{-i(\mu+1)\eta\} - iv^{-1}(\mu-1)\Big\}.$$
$$.\ \ .\ \ .\ \ .\ \ (21)$$

Similarly, when $\xi = \eta$ (20) becomes

$$A(\mu^2 - 1) = C_1 \left\{ (\mu^2 - 1)\chi^{-1} \exp i(\mu+1)\eta + iv^{-1}(\mu-1) \exp i(\mu+1)\eta \right.$$
$$\left. - iv^{-1}(\mu-1) \right\}$$
$$+ C_2 \left\{ (\mu^2 - 1)\chi^{-1} \exp\{-i(\mu-1)\} - iv^{-1}(\mu+1) \exp\{-i(\mu-1)\eta\} \right.$$
$$\left. + iv^{-1}(\mu+1) \right\}. \quad . \quad . \quad . \quad (22)$$

21. The constants C_1, C_2 are thus determined, and the solution of the proposed problem, in terms of the single complex constant χ, is fully indicated. The results, moreover, are not limited in their scope to the acoustical type of problem which has so far claimed our attention; in the form (18), (21), (22) they would be equally applicable to a cloud of light-scattering molecules or particles, whether the scattering is accompanied by absorption or not: it would only be necessary to assign to χ its proper value in each case.

22. There are two cases in which the results of § 20 assume a specially simple form; in the one case L is very small compared with λ, that is, η is very small; in the other case L (or η) is infinite. When η is very small, it is most convenient to go back to the integral equation (16), which now takes the form

$$\chi^{-1}B + A + v^{-1}\int_0^\eta B'd\xi' = 0.$$

This shows that, to our degree of approximation, B is a constant, so that the above definite integral $= B\eta = BvL$, and we get

$$B = -\frac{A\chi}{1 + \chi L}.$$

The waves emitted by the total of the vibrators are now by (14)

$$\psi'', \psi''' = BL \exp i(pt \mp vx)$$
$$= -\frac{A\chi L}{1 + \chi L} \exp i(pt \mp vx) \left. \right\} \quad . \quad . \quad . \quad (23)$$
$$vL \text{ or } 2\pi L/\lambda \text{ being small.}$$

23. If we now introduce the condition that through the lamina $0 < x < L$ the secondary vibrators are distributed like gas-molecules, (13) holds good and (23) takes the form

$$\psi'', \psi''' = -Aw\{1 + w \exp i(\tfrac{1}{2}\pi - \gamma)\}^{-1} \exp i(pt \mp vx + \tfrac{1}{2}\pi - \gamma)$$

where $w \equiv 2\pi\sigma \sin \gamma/v^2$,

and $\sigma = vL$, the number of vibrators per unit *area* of the

lamina. The last written result can be readily put in the form

$$\boldsymbol{\psi}'',\ \boldsymbol{\psi}''' = -Aw(1+2w\sin\gamma+w^2)^{-\frac{1}{2}}\exp i(pt\mp x+\tfrac{1}{2}\pi-\gamma+\epsilon)$$

$$\text{where } \frac{\sin}{\cos}\,\epsilon \equiv \frac{w\cos\gamma,\ 1+w\sin\gamma}{\sqrt{(1+2w\sin\gamma+w^2)}}. \qquad (24)$$

24. If the vibrators are tuned as resonators, $\gamma=\frac{1}{2}\pi$ and (24) becomes identical with (9), (9 a). Now in the deduction of (24) no limit has been imposed on the closeness of packing of the vibrators, except the condition that their aggregate bulk is but a small fraction of the space through which they are distributed. If we can conceive of the vibrators as indefinitely small, and as retaining always their property of scattering without absorbing wave-energy, the number σ per unit area of the lamina may be as great as we please without invalidating (24) or its particular form (9), (9 a). The restriction provisionally imposed in § 10 is thus found to be unnecessary.

25. From (9) together with (5) a good idea is gained of the change of behaviour of a sheet (or thin lamina) of resonators as the number σ per unit of area is gradually increased. The proportion of the incident energy contained in the regularly reflected beam is

$$\frac{4\pi^2\sigma^2/v^4}{(1+2\pi\sigma/v^2)^2},$$

which gradually approximates to unity as σ is increased. At the same time the proportion of the incident energy which becomes diffusely scattered is $v^2/\pi\sigma$ times this expression, that is

$$\frac{4\pi\sigma/v^2}{(1+2\pi\sigma/v^2)^2},$$

which becomes insignificant both for very small and for very large values of σ; attaining its maximum when $2\pi\sigma/v^2=1$; that is when this scattered energy is half the energy of the regularly reflected train.

26. A further point should now be remarked : if the secondary vibrators become so closely crowded together that the freedom of position for any given one is sensibly restricted by the presence of the others, the *irregularity* of the distribution will no longer be complete, and the proportion of energy scattered will be less. As the swarm of vibrators becomes more and more compressed, though retaining as complete an irregularity as still remains possible, the distribution will resemble that of the molecules of a liquid rather

than of a gas, and the diffusely scattered energy may then be small compared with $v^2/\pi\sigma$ times the energy regularly reflected. Thus the lamina, with increasing density, may be expected to approximate in behaviour to a specular reflector more rapidly than is indicated by the theory in its simplest form: true absorption, as before, being absent.

27. None of the incident plane-wave energy is diffusely scattered by an extensive *ordered* arrangement of secondary vibrators, such as that investigated by Lord Rayleigh * (who points out, however, that the scale of the arrangement must not be too great if we wish to avoid complications from spectra of various orders). This leads to a considerable divergence between the properties of plane assemblages of vibrators, according as the distribution is ordered or wholly irregular. For in the latter case, when the vibrators are tuned as resonators, (9), (9 *a*) indicate that the secondary plane waves emitted are always *directly opposed* in phase to the incident train. Since the vibrators *ex hypothesi* absorb no energy, there must evidently be another energy-term in question ; and this term, as we have seen, corresponds to the disturbance irregularly scattered. When the arrangement of resonators is orderly and not too open, so that the only secondary disturbances are normally propagated plane waves, the phase of these must always be such as to keep the total wave-energy unchanged.

The second part of this paper deals in some detail with the aspects of the problem of § 18 when the thickness L is infinite, as well as with the modifications which have to be made in the various formulæ when it is desired to apply them to the solution of optical problems.

Boar's Hill, Oxford,
6th March, 1915.

LXVII. *A New Type of Ion in the Air.* By J. A. Pollock, *D.Sc., Professor of Physics in the University of Sydney*†.

Introductory.

IN an address to the members of Section A of the Australasian Association for the Advancement of Science at Brisbane, in 1909, I mentioned that observations of atmospheric ionization, made at the Physical Laboratory of the University of Sydney, indicated the presence in the air of

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* Phil. Mag. *loc. cit.*
† Communicated by the Author.

an ion with a mobility intermediate between that of the small gas ion and that of the large ion of Langevin. Under average atmospheric conditions this new ion has a mobility of about 1/50, and like the Langevin ion its mobility depends on the hygrometric condition of the air. The large ion, however, judging from cloud condensation experiments, retains its stability even if the vapour-pressure becomes slightly greater than that of saturation for a plane water surface, irrespective of the temperature, whereas the ion of intermediate mobility disappears if the vapour-pressure exceeds a certain value, less than that of saturation for summer temperatures.

In a paper on the Nature of the Large Ion*, recently published in the Philosophical Magazine, I put forward the view that in the Langevin ion we have an instance of the adsorption in the liquid state of water-vapour by a rigid nucleus, as from the relation between mobility and vapour-pressure it was deduced that the adsorbed fluid had a latent heat very little different from that of water. In this paper I propose to show that the ion of intermediate mobility consists of a rigid core surrounded by adsorbed moisture which, on the whole evidence, is certainly not in the liquid condition.

Trouton†, in 1907, made the interesting discovery that there are two modes of condensation of water-vapour on rigid surfaces. If special precautions are taken in drying the surfaces, on exposure to water-vapour, adsorption occurs as a dense atmosphere of water molecules, in a state, no doubt, intermediate between that of a gas and that of a liquid. At any rate, a change to the liquid condition somewhat abruptly takes place, in these circumstances, when, according to Trouton, the humidity is about 50 per cent. in the case of glass, and about 90 per cent. in that of shellac.

In the intermediate ion, the state of the fluid, doubtless, corresponds to that of the moisture condensed at low pressures on carefully dried surfaces in Trouton's experiments. The two classes of ions thus appear to illustrate in a somewhat striking way Trouton's discovery of the two modes of condensation. Further, the intermediate ion is not to be found when the vapour-pressure exceeds 17 millimetres, and it seems not unlikely that at a critical pressure, by a change in the state of the fluid surrounding the nucleus, it develops into the large ion of Langevin.

* Pollock, Phil. Mag. April 1915.
† Trouton, Proc. Roy. Soc. A, lxxix. p. 383 (1907); Chem. News, xcvi. p. 92 (1907).

Measurement of Mobility.

The mobility of the ions was determined by passing a steady stream of air through a cylindrical condenser, and measuring the leak between the electrodes for various differences of potential between them, as in Zeleny's[*] investigation of the mobility of the small ions, and Langevin's[†] original determinations of the mobility of the large ones. The condenser consisted of a brass tube, 164 centimetres long, provided with an axial electrode of the same length; the diameter of the inside of the tube was 3·65, and that of the inner rod 0·66 centimetre. The inner electrode was divided into two sections, insulated from each other: the portion at the mouth of the tube had, on different occasions, the lengths 3·8, 7·7, and 25 centimetres, the distance between the two sections being 4 millimetres in all cases. This brass tube with its inner electrode will be called the testing-pipe.

In my experience the ionization seems more uniform if the air passes through some length of tubing before being used, and for the great majority of the observations given here, the air, before entering the testing-pipe, travelled first through 28 metres of iron piping and then through 9 metres of galvanized iron pipe, the diameters of the pipes being 4·5 and 7·7 centimetres respectively. In all but the determinations at humidities about 90 per cent., the air was from the compressed supply of the laboratory, which is fed by a Sturtevant blower worked by a motor and storage-cells. The blower was open to the air of the laboratory workshop, which in turn was kept open to the outer air, the measurements being ordinarily made at night. Control experiments with air drawn directly into the testing-pipe showed that the piping impressed no peculiarity on the mobility determinations, though, no doubt, diminishing the ionization.

The estimation of mobility requires the determination of a critical voltage in connexion with a series of ionization currents, and although the natural ionization is very variable, at times the measurements agreed among themselves sufficiently well for the purpose of the calculation. Fig. 1 represents one of the best examples of the type of results obtained on these occasions when the long section of the inner rod was attached to the electrometer, while fig. 2, drawn from similarly accordant measures, shows the form of the plot of the observations when the electrometer was joined to the short section of the inner electrode[‡].

[*] Zeleny, Phil. Trans. A. cxcv. p. 193 (1900).

[†] Langevin, *Comptes Rendus*, cxl. p. 232 (1905).

[‡] For further observational detail see Journ. and Proc. Roy. Soc. N. S. Wales, p. 61 (1909).

Fig. 1.
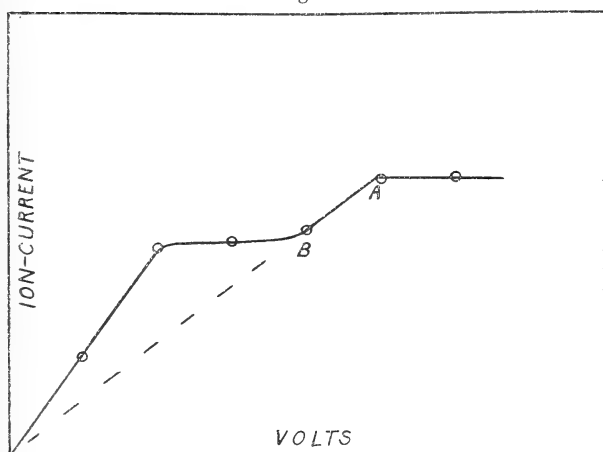
Fig. 2.
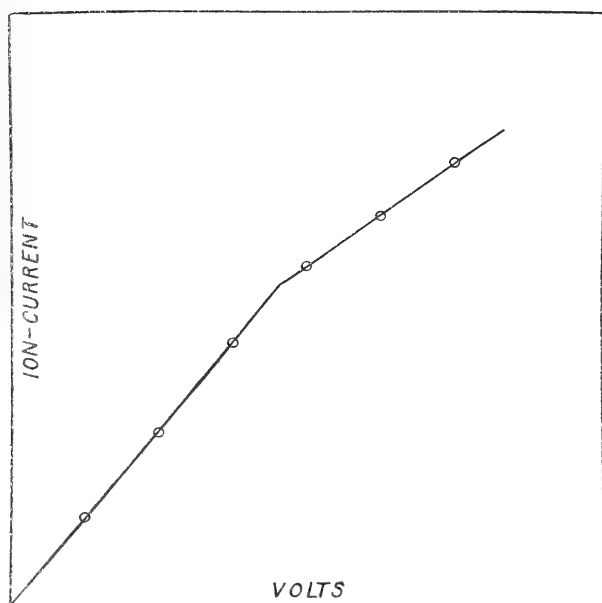
Owing to the variable nature of the ionization the lie of the lines in the diagrams is ordinarily subject to some uncertainty, but the determinations of the humidity are not sufficiently satisfactory to make any attempt to weight the

measures advisable in the present instance. The mobilities have been calculated, without correction, from the formula

$$u = \frac{(\log_e b/a)Q}{2\pi V X},$$

where b/a is the ratio of the radii of the tube and inner rod, Q the air-stream in cubic centimetres per second, V the critical potential difference between the electrodes corresponding to a special value of X, the distance of an end of an electrode from the mouth of the tube.

In the curves like that in fig. 1 there are two critical voltages. The upper one A, the minimum potential difference for which the current has its constant value, represents the voltage for which the extreme ions of a certain class just reach the further end of the long electrode, counting from the mouth of the tube, the extreme ions being those which enter the tube at a distance b from its axis. The ions here are the large ions of Langevin.

The other critical potential B gives the voltage at which the extreme ions of another class just fail to reach the near end of the same electrode.

When the short section of the inner rod, at the mouth of the pipe, was attached to the electrometer, only one critical potential occurs, as shown in fig. 2. The value here is the voltage when the extreme ions of a certain class just reach the further end of this short electrode. It was found that the critical voltages in the two latter cases refer to the same class of ions, the calculated value of the mobility being independent of the particular arrangement of apparatus which was used. It is the ions of this class which form the subject of this paper.

The values of the mobilities which have been determined are given in Table I., T being the temperature in centigrade degrees, p the vapour-pressure, p/P the relative humidity, and N the number of these ions per cubic centimetre under the circumstances of the experiment. A considerable number of measurements were made with artificially dried air when the value of the humidity was about 33 per cent. To keep the table within reasonable limits only the extreme measures for these humidities have been given, but the omitted results are included in figs. 3 and 4. The numbers have been reduced to standard pressure on the assumption that at constant temperature the mobility varies inversely as the density of the air, but this and the corresponding temperature correction, calculated on whatever basis, are too small to be of the slightest consequence in connexion with the present measures.

The positive and negative signs in the table indicate the electrical class of ions to which the respective observations refer, but it may be stated here that no definite difference between the mobilities of the positive and negative ions can be deduced from the results.

TABLE I.

$1/u_{760}$.	T.	p.	p/P.	N.	Length of electrode. cm.
			per cent.		
15·0 +	21·8	0·78	4	130	3·85
15·2 +	20·8	0·73	,,	158	,,
17·6 −	19·7	0·68	,,	78	,,
38·9 −	18·4	4·97	31·5	...	160
49·2 +	24·8	7·33	,,	...	7·7
43·0 −	20·0	5·92	34·0	...	3·85
53·0 −	21·3	6·41	,,	...	,,
49·8 −	20·9	11·67	64	...	160
53·0 −	20·9	10·82	59	...	,,
53·4 +	24·5	14·18	62	...	25
54·8 −	15·3	6·66	51	...	160
55·1 +	20·4	13·29	75	426	,,
56·2 +	20·1	11·29	64	114	,,
60·1 +	21·6	14·11	73	156	,,
63·3 +	23·9	15·66	71	...	25
65·3 +	22·6	15·43	76	291	160
68·4 +	21·0	13·16	71	281	,,
86·4 +	24·3	15·58	69	...	25
91·0 +	24·2	14·40	64	...	,,
110·3 +	22·1	13·89	70	514	3·85
124·2 −	22·2	14·35	72	1346	,,
137·4 −	22·2	15·43	78·5	1144	3·85
139·9 −	24·5	16·67	73	174	7·7
156·1 −	23·4	14·87	69·5	458	,,
157·3 +	22·8	14·06	68	1165	,,
350 +	19·5	16·88	89·1	...	25
407 +	19·7	17·09	,,	...	,,

Discussion of Results.

In my previous paper, on the nature of the large ion, I showed by a simple thermodynamic argument that a formula of reduction for adsorption observations at different temperatures is contained in the expression $(p_1/p_2)_m = (\mathrm{P}_1/\mathrm{P}_2)^{1\,n}$. p and P are, respectively, the values of the pressure of the vapour in equilibrium with the adsorbed fluid, and the saturated

vapour-pressure for a plane water surface at the same temperature, and n is the ratio of the latent heat of vaporization of water to that of the adsorbed fluid surrounding the core of the ion. m is the mass of the adsorbed fluid, or in the present application, the mobility of the ion reduced to constant air density. The suggestion was also made that a clue to the condition of the adsorbed fluid might be obtained in the value of n found necessary in any instance for the reduction of adsorption observations.

In the case of the large ions, unity, to an accuracy perhaps greater than one in a hundred, is the value of n which gives the best fit to a line of the points representing the mobilities, determined at different temperatures, when plotted against vapour-pressures. In other instances mentioned in the paper n is also unity. No heat change due to a variation of surface energy is involved in the value of n, so in these cases where $n = 1$, as the heat per unit mass necessary to annul a temperature change due to the mere alteration of state is the same as that required to keep the temperature constant when water evaporates, I think we may definitely conclude that the molecules in the contained or adsorbed fluid are in the same condition of aggregation as those of water.

Now with regard to the intermediate ion, its mobility also depends on the hygrometric condition of the air ; this ion, then, as well as the large one is composed, partly at least, of water molecules. But the mobilities are as sixty to one, so, if no other cause of difference exists, the moisture forming the ions must be in very different states in the two instances.

If such is the case, the observations of the mobilities of the intermediate ion should only fall into line in relation to the vapour-pressure if reduced according to the formula $(p_1/p_2)_m = (P_1/P_2)^{1/n}$, with some value of n greater than unity. Unfortunately the results are not accordant enough to enable the value of n to be determined in this way with any accuracy, and as $(P_1/P_2)^{1/n}$, within the limits of the observations, is so nearly equal to unity for even small integer values of n, all that can be done is to compare plots of the measures in the extreme cases, firstly when n is taken as unity, and secondly when it is put equal to some large number. In the first instance, when $n = 1$, by the preceding formula the mobility will be constant if $p_1/P_1 = p_2/P_2$. Accordingly the mobilities are to be plotted against the relative humidities, as in fig. 3, and if the points fall into line it is to be taken as evidence that the adsorbed fluid is in the liquid condition. On the other hand, when n equals some

large number, the mobility will be constant only if $p_1 = p_2$, so the mobilities are to be entered against the vapour-pressures. If the plot here is better than in the previous case it

Fig. 3.

MOBILITY—RECIPROCAL
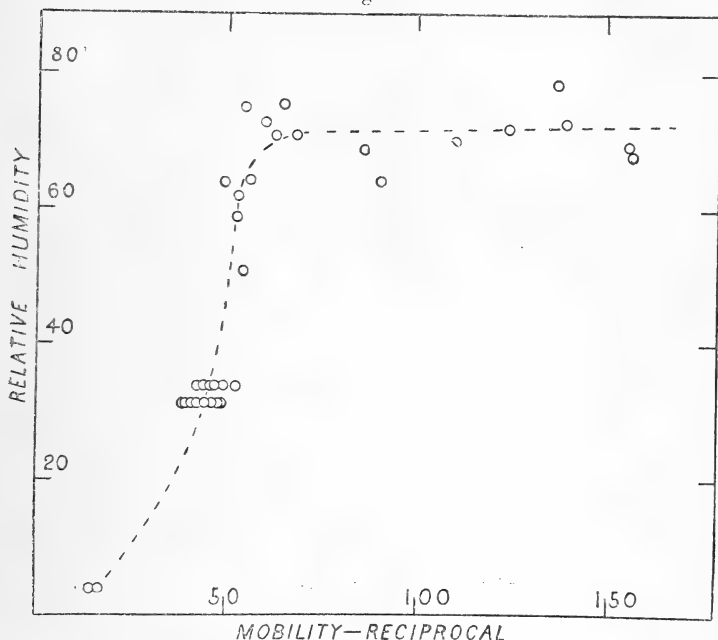
is to be considered that the fluid is in the state of a dense vapour rather than in that of a liquid. Such a plot is shown in fig. 4.

An inspection of the figures shows that the fit to a line is, for certain groups of observations at least, better in fig. 4 than in fig. 3. The fit might, perhaps, be slightly improved if n were taken equal to a smaller integer for the determinations at higher, than for those at lower pressures, which would indicate that the latent heat of the adsorbed fluid becomes greater as its density increases. But the general want of accord amongst these pioneering observations is so considerable that the present line of argument is not conclusive, and cannot be taken as more than supporting the assumption that the intermediate ion consists of a rigid nucleus surrounded by a dense atmosphere of water-vapour, rather than by water in the liquid state. Further evidence is available, and the assumption is greatly strengthened by a consideration of the circumstances connected with the disappearance of the ion.

2 T 2

Instability of the Ion.

The curve in fig. 4 shows that at a pressure of about fifteen millimetres the mobility of the ion increases very rapidly with increase in the value of the vapour-pressure.

Fig. 4.

MOBILITY—RECIPROCAL
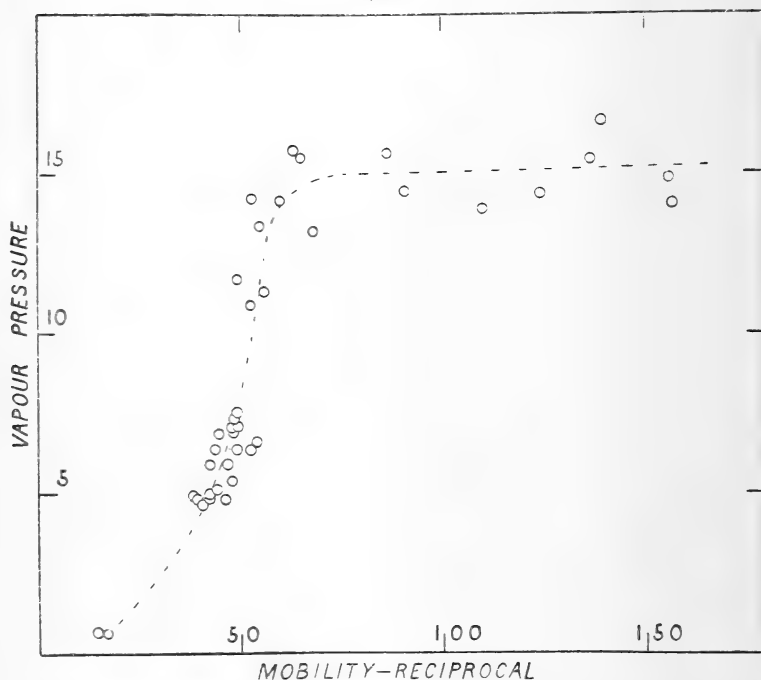
On many occasions, as already mentioned, successful simultaneous observations of the intermediate and large ions were obtained, but with vapour-pressures exceeding seventeen millimetres, while the observations of the large ions were equally good, all trace of the intermediate ion disappeared. To be quite definite, above this pressure no evidence was ever found of any class of ions with a mobility between 1/50 and 1/3000. Disintegration of the ion at a critical vapour-pressure is unlikely, and it is much more probable, assuming a rigid nucleus, that the adsorbed fluid is in the condition of a dense vapour, and that at the critical pressure it changes its state to that of a liquid, like the moisture adsorbed by glass and shellac in Trouton's experience.

Such a change means a decrease in the energy of the aggregation, and is to be expected when the molecules of

water-vapour round the nucleus become sufficiently tightly packed. The advent of a liquid surface involves a diminished rate of molecular escape ; rapid condensation will therefore occur, with a decreasing unit-surface energy, until further increase in the size of the ion means an increase in the total energy of the mixture of ions and vapour. The final result is no other than the large ion of Langevin, where, as I have shown, the surrounding moisture is in the liquid state.

There is independent evidence from cloud condensation experiments that the large ion has a rigid core, but, as yet, no such evidence exists in the case of the intermediate ion. If, however, the intermediate ion becomes the large one by a change of fluid state only, it must have the same nucleus as the larger aggregation. The mobility which the core alone would have may be estimated by extrapolation in connexion with the curve in fig. 4. Judging from the comparatively large value which is indicated the nucleus may be, at most, a collection of not many molecules. In this connexion it is interesting to remember that the mobilities of the fully developed large ions, under given atmospheric conditions, appear to lie within narrow limits; the explanation depends, no doubt, on some characteristic of the nuclei.

Sutherland, in his paper on the Ions of Gases in the Philosophical Magazine for September 1909, definitely makes the suggestion of an ion of intermediate mobility " consisting of an envelope of vapour, such as that of H_2O, surrounding a small ion which is the central nucleolus," and he applies the conception to the experiments of Moreau on the cooled gases of flames sprayed with electrolytic solutions. The discussion in this present paper is on different lines to that so ably developed by Sutherland.

Summary.

A description is given of certain characteristics of an ion in the air with a mobility intermediate between that of the small gas ion and that of the large ion of Langevin.

The mobility is found to depend on the water-vapour pressure rather than on the relative humidity.

Both the intermediate and large ions exist in the air at the same time provided the vapour-pressure is below seventeen millimetres. Above this pressure only the large ion is found.

On the whole evidence it seems probable that the intermediate ion consists of a rigid nucleus enveloped by a dense atmosphere of water-vapour. The mass of the ion becomes greater as the vapour-pressure increases, until at a critical

pressure the adsorbed fluid assumes the liquid state, and the aggregation develops, by the rapid condensation which ensues, into the large ion of Langevin.

The intermediate and large ions thus appear to form a somewhat striking illustration of Trouton's discovery of the two modes of condensation of water-vapour on rigid surfaces.

The Physical Laboratory,
        The University of Sydney,
                January 8, 1915.

LXVIII. *The Brightness of Intermittent Illumination.*   *By* M. O. SALTMARSH, *B.A.*, *Demonstrator in Physics at Bedford College, London**.

WHEN light from a constant source falls on a surface, the illumination over a small area is uniform.   If the source is screened from the surface at regular intervals of time, the illumination will appear intermittent and flickering, unless the interval of time during which the light is screened, be small enough.   For a particular value of this interval of time, the flickering of the illumination will just cease, and in this case the visual impression received when the screen is illuminated will be just carried on with equal intensity over the period of darkness, so that the illumination is apparently uniform.   If the time of complete darkness is less than this value, and the visual impression which is carried on from one time of illumination overlaps that received during the next time of illumination, the eye, while still retaining the effects of one stimulus, will be acted on by another.

Is the brightness, therefore, that corresponding to the new stimulus alone ? or, does the residual effect of the preceding one influence it in any way ?

It was with a view to settling this point that the observations described in this paper were made.

A photometer bench, about 2·5 metres long, was used and it was fitted with a smoothly running upright carrying a Bunsen photometer.   An electric lamp was placed at either end of the bench, and in front of one, a black cardboard disk was rotated about a horizontal axis through its centre by means of an electric motor.

The number of revolutions of the disk per second was

determined by a revolution counter working on the shaft to which the disk was attached.

Equal portions of sectors were cut out of the disk at even distances round a ring, forming a number of equal apertures, and the same number of equal shutters; the apertures were not necessarily equal to the shutters in size. The outer diameter of the ring was 40·3 cm. and the inner 24·3 cm. The disk was placed in such position that as it revolved, the lamp was alternately completely open to or completely screened from the photometer.

The fraction of the light cut off when the disk revolves is the ratio of the size of a shutter to the size of a shutter and aperture together. Since the lamp itself was not a line of light, the times of complete darkness or full brightness were less than that taken for a shutter or aperture to pass respectively.

The time curve of the flux of light on the photometer for a disk with equal apertures and shutters is of the shape shown in the diagram.
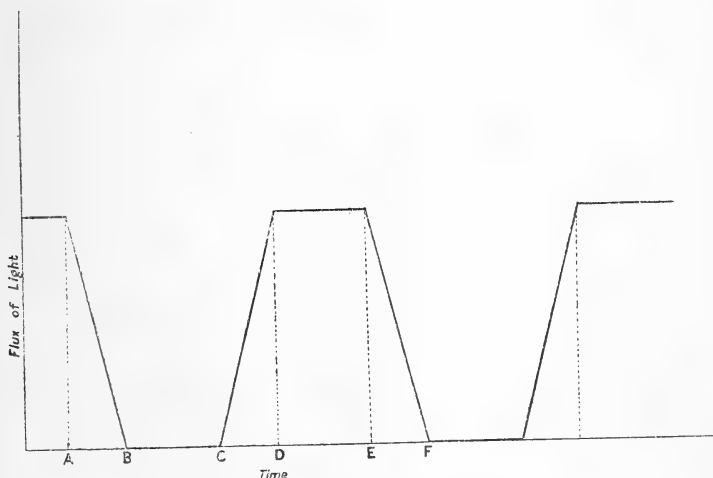
AB is the time taken for one edge of a shutter to pass from one side of the light to the other, and so completely obscure it; CD is the time taken for one edge of an aperture to pass from one side of the light to the other, and so completely open it. It was easily determined by measuring what fraction of an aperture was occupied by the luminous filament of the lamp.

The time taken for this fraction to pass in front of the lamp was subtracted from the time taken for a shutter to

pass, and this gave the time of complete darkness, BC. The time DE, during which the illumination was uniform, was obtained in the same manner; and the total time of illumination was given by CF.

The observations were made as follows:—The lights were adjusted at equal heights from the bench and at a distance of about 190 cm. apart; the photometer was set between them at the same height in the position of equal illumination, and the distances from the lamps measured to $\frac{1}{10}$ mm.; the sides of the spot were reversed, and the photometer was set again. This was repeated independently three times for the same distance apart of the lights, and the means of the distances a and b of the lamps from the photometer were taken for one side of the grease spot, and the means a' and b' for the other side were taken.

The ratio $\dfrac{I_1}{I_2} = \dfrac{aa'}{bb'}$ was calculated. The light I_1 was then moved in 10 cm. and the process repeated, giving another value for $\dfrac{I_1}{I_2}$. The mean of the two was taken.

For the whole set of observations the mean difference of a value from the corresponding mean value was ·57 per cent. This represents the average error of the observations. If the brightness, when the disk is rotating, is $\dfrac{1}{\kappa}$ of what it is when the photometer is illuminated by the full light from the lamp, the observation will give a value of κ.

If the residual visual impression does not alter the apparent brightness of the surface of the photometer, κ will also represent the fraction of the whole light which is transmitted through the rotating screen. If it does, κ will not be the same as this fraction, and the illumination will appear flickering when the residual visual impression only partly overlaps the next stimulus. Thus flickering would disappear for a certain speed of opening and closing the shutter, and would reappear again for a higher speed.

In the case of equal-sized shutters and apertures, the ratio of the duration of full brightness to total darkness is 1. With shutters which are smaller than the apertures the ratio is greater than 1, and there would be more overlapping; while with apertures smaller than the shutters the ratio is less than 1, and there would be less overlapping.

In the tables I_1 is the intensity of the unscreened light and I_2 that of the screened. I_1 was about 18·7 candle-power, as compared with a 10 candle-power pentane standard.

When the speed of the disk was not great enough the appearance of the photometer was flickering. It was found possible to obtain consistent values when the flickering was not too pronounced. In these cases, there was no overlapping of the visual impressions. Those observations in which the appearance was flickering are marked with an *f*.

Table I. shows results obtained with a disk having 4 shutters and 4 openings all equal in size. The fraction of light transmitted by the disk was ·500.

<div align="center">TABLE I.</div>

Time of total darkness.	Time of full brightness.	$\dfrac{I_1}{I_2}$.	$\dfrac{I_1}{\kappa I_2}$	κ.
·0144 sec.	·0144 sec.	·7694	1·549	·497 *f*
·0116	·0116	·7723	1·556	·497 *f*
·00774	·00774	·7736	1·534	·504
·00620	·00620	·7649	1·511	·506
			Mean ...	·501

Table II. shows results obtained with a disk having 8 apertures and 8 shutters of equal size. The fraction of light transmitted is ·500.

<div align="center">TABLE II.</div>

Time of total darkness.	Time of full brightness.	$\dfrac{I_1}{I_2}$	$\dfrac{I_1}{\kappa I_2}$.	κ.
·00847 sec.	·00847 sec.	·8211	1·6255	·504 *f*
·00653	·00653	·8211	1·646	·497
			Mean ...	·501

In the two above sets of observations, no reappearance of flicker was observed as the speed of the disk was increased; but in both cases the time of darkness was the same as the time of full brightness, and the duration of visual impression might be dependent upon the time for which the eye is exposed to light, in such a way that, if the latter were diminished, the former would be also, and there would be less chance of overlapping with shutters and apertures of equal size. A disk in which the apertures were 3 times the size of the shutters was therefore used, there being 4 apertures and 4 shutters. The fraction of light transmitted by this disk was ·750.

The results are shown in Table III.

<div align="center">TABLE III.</div>

Time of total darkness.	Time of full brightness.	$\dfrac{I_1}{I_2}$.	$\dfrac{I_1}{\kappa I_2}$.	κ.
·0064 sec.	·0292 sec.	·8185	1·105	·741 f
·00273	·01269	·8185	1·090	·751
·00241	·01483	·7904	1·054	·749
			Mean ...	·747

If the apertures are smaller than the shutters there might be less chance of overlapping: The results in Table IV. were obtained with a disk with 4 shutters and 4 openings, the shutters being 3 times the openings; the fraction of light transmitted through this disk is ·250.

<div align="center">TABLE IV.</div>

Time of total darkness.	Time of full brightness.	$\dfrac{I_1}{I_2}$.	$\dfrac{I_1}{\kappa I_2}$.	κ.
·0326 sec.	·00748 sec.	·7904	3·175	·249 f
·0135	·00310	·7904	3·148	·251
·0118	·00270	·7904	3·144	·251
			Mean ...	·2503

No reappearance of flicker was observed.

It will be noticed in the tables that the time of total darkness, when the appearance is flickering, becomes less when the fraction of light transmitted through the disk, and therefore the illumination, is greater. This is in agreement with the results obtained by Porter[*].

<div align="center">*Conclusion.*</div>

From the above values of κ it can be concluded that the residual visual impression carried on from one time of illumination to the next and overlapping it makes no difference to the apparent brightness.

I should like to record my thanks to Dr. Womack, of Bedford College, for suggesting this matter as a subject for investigation.

Bedford College,
Regent's Park, N.W.,
March 9, 1915.

* Porter, Proc. Roy. Soc. 1902.

LXIX. *Remarks regarding the Series Spectrum of Hydrogen and the Constitution of the Atom. By* L. VEGARD, *Dr. Phil., Lecturer of Physics at the University of Christiania* *.

IN the number of the Phil. Mag. for Jan. 1915, Dr. H. Stanley Allen has published two interesting papers, where he considers the case in which the circulating electrons of the atom, in addition to the electrical forces, are acted on by a magnetic field equivalent to that of an elementary magnet placed at the centre and with its axis perpendicular to the plane of the orbit.

Generally, he finds that the magnetic effects " are not in themselves sufficient to account for more than a small fraction of the effect that would be necessary to give the observed distribution of lines in spectral series."

In the case of hydrogen, however, he finds that the deviation from the Balmer formula as found by Curtis would be explained, when in certain states of motion the electron was acted on by the field of an elementary magnet with a moment of 5 or 6 magnetons and placed at the centre, and he states that " in support of the view that the core contains 5 magnetons we have the fact first pointed out by Chalmers that the magnetic moment produced by an electron moving in a circular orbit with angular momentum of $\frac{h}{2\pi}$ is exactly 5 magnetons."

Regarding this last point I should like to make a few remarks.

The 5 or 6 magnetons which are necessary to explain the deviations from the Balmer formula in the way proposed by Dr. Stanley Allen must be due to a magnetic system near the centre, and are of course not to be identified with the 5 magnetons produced by the light-emitting electron in the normal state of the atom; and if the explanation of Dr. Stanley Allen is correct, it would have important consequences with regard to our conception of the inner nucleus.

The inner magnetic system might either be produced by circulating electrons or by the rotation of the positive nucleus.

The angular momentum μ of a sphere is $\frac{2}{5}Ma_0^2\omega$, where M is the mass, a_0 the radius, and ω the angular velocity. The

magnetic moment $M_g = \frac{1}{2}\frac{e}{M}\mu$ and the kinetic energy $\frac{1}{2}\mu\omega^*$. If the mass of the nucleus is of purely electromagnetic origin, its radius is equal to $\frac{2}{3}\frac{e^2}{M}$, when the charge is supposed to be on the surface of the nucleus. For a volume distribution we can assume the formula to give a radius of the right order, or about 10^{-16} cm. for the hydrogen nucleus.

In order to get a magnetic moment of 5 magnetons we should have to assume an angular momentum of $1800\frac{h}{2\pi}$, and the number of rotations (ν) in unit time would be $4\cdot6\times10^{31}$, and the kinetic energy $2\cdot8\times10^{+8}$ erg, or about 10^{19} times the energy of the outer electron in the normal state of the atom. As long as we know so little about the interior of the atom we are perhaps not allowed to say that the existence of such rotations and the enormous store of energy are impossible, although there seems no special reason for the assumption unless we would suppose that the internal energy of the atom which is brought to light through the atomic disintegration is to be of a rotational nature, and that the rotations are preserved also for the lighter elements like hydrogen.

Let us next consider the case in which the inner magnetic system is composed of $(N-1)$ electrons circulating round the nucleus with a positive charge $+Ne$. If the angular momentum of all inner electrons $\sum\limits_{1}^{N-1} ma_i^2\omega_i$ is equal to $\frac{h}{2\pi}$, they would produce a magnetic moment of 5 magnetons.

Let all electrons form one ring, then

$$a_i = \frac{a}{(N-1)^2(N-\frac{1}{4}S_{N-1})}$$

and

$$W_i = (N-\tfrac{1}{4}S_{N-1})^2(N-1)^3W.$$

a_i and W_i are radius and energy of inner ring, a and W the corresponding quantities for the light-emitting electron in the normal state.

In order that the inner system shall act electrically on the outer electron as a single charge $+e$, $\frac{a_i}{a}$ must be a small quantity. In fact, $\frac{a_i}{a}$ diminishes rapidly with increase of N. Thus with an inner ring of 4 electrons $\frac{a_i}{a}=61$, and $W_i=940\,W$,

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* It is supposed that the inner nucleus can be treated as a charged solid body.

and we see that the energy of the magnetic system also in this case would be very great compared with that of the light-emitting electron in the normal state.

Even if we take it for granted, however, that the assumption of an inner magnetic system is a legitimate one, we should still meet with the difficulty that, according to Dr. Stanley Allen, the magnetic moment must vary considerably with the state of motion of the light-emitting electron. In fact, it is assumed that for the state of motion corresponding to an angular momentum of $\dfrac{h}{\pi}$ the magnetic moment of the inner system is equal to zero, while for the stationary circles of greater momentum the magnetic moment is 5 magnetons.

Dr. Allen gives no indication as to how the passage of the electron from one stationary circle to the next can increase the magnetic moment from 0 to 5 magnetons. With certain modifications of Dr. Allen's assumptions we might, however, in quite a formal way explain the formula of Curtis through the effect of an internal magnetic field.

We suppose the inner magnetic system to be produced by circulating electrons, and that the inner magnetic system and the outer electron maintain a constant difference of momentum equal to $\dfrac{h}{\pi}$,

$$\mu - \mu_i = \frac{h}{\pi},$$

putting

$$\mu = \frac{h\tau}{2\pi}$$

$$\mu_i = \frac{h}{2\pi}(\tau - 2),$$

and the magnetic moment of the inner system would be

$$M_g = \frac{h}{4\pi c^2}\frac{e}{m}(\tau - 2) = 5(\tau - 2) \text{ magnetons,}$$

where c is the velocity of light*.

Now Dr. Allen has deduced the following general formula for the magnetic influence on the spectrum:

$$\frac{\nu}{N} = \frac{1}{\left(\tau_2 + \dfrac{B_2}{\tau_2^2}\right)^2} - \frac{1}{\left(\tau_1 + \dfrac{B}{\tau^2}\right)^2},$$

where

$$B = \frac{16\pi^3 me^3}{h^3} M_g = \frac{4\pi^2 e^4}{h^2 c^2}(\tau - 2).$$

* M_g and e are given in electrostatic units.

Putting $\qquad B_0 = \dfrac{4\,\pi^2 e^4}{h^2 c^2}$ and $\tau_2 = 2$, we get $B_2 = 0$ and

$$\frac{\nu}{N} = \frac{1}{4} - \frac{1}{\left\{\tau + B_0\left(\dfrac{1}{\tau} - \dfrac{2}{\tau^2}\right)\right\}^2}.$$

This formula is somewhat different from that found by Dr. Stanley Allen, but it will equally well represent the observed facts.

For the six lines considered in Dr. Allen's paper we get:

τ...............	3.	4.	5.	6.	7.	8.
$\left(\dfrac{1}{\tau} - \dfrac{2}{\tau^2}\right)$......	1/9	1/8	3/25	1/9	5/49	3/32

It happens that for these lines $\left(\dfrac{1}{\tau} - \dfrac{2}{\tau^2}\right)$ comes out practically constant equal to 1/9, and we get the formula

$$\frac{\nu}{N} = \frac{1}{4} - \frac{1}{\left(\tau + \dfrac{B_0}{9}\right)^2},$$

which has exactly the same form as the empirical formula found by Curtis. Using the values $\dfrac{e}{h} = 7\cdot27 \times 10^{16}$ and $e = 4\cdot78 \times 10^{-10}$, we find $B_0/9 = 5\cdot9 \times 10^{-6}$, while the corresponding constant in Curtis' formula is equal to $6\cdot9 \times 10^{-6}$.

Thus the deviation from the Balmer formula would be satisfactorily explained through the magnetic influence of the inner core, when a constant difference of momentum of $\dfrac{h}{\pi}$ is supposed to be maintained between the outer and inner system.

It may be granted that in dealing with atomic structure we have a fairly great freedom for making assumptions, but still I think we ought to hesitate in assuming *any connexion* between the outer and inner system which would change the magnetic moment of the latter from zero to 5 magnetons when the outer electron passes from the circle corresponding to $\tau = 2$ to that for which $\tau = 3$.

We have previously seen that the magnetic core of 5 magnetons, whether it consists of a rotating nucleus or a system of electrons, would store an energy which is enormously

greater than the kinetic energy of the outer electron ; and it seems hardly possible to suppose a system with so much energy to be essentially affected by the passage of the outer electron from one stationary circle to the next ; for it must be kept in mind that in the passage of the electron from $\tau = 2$ to $\tau = 3$ the inner system should take up the whole energy involved in the production of the magnetic field of 5 magnetons.

As, however, the assumption of a mutual connexion between the inner core and the outer electron seems essential for the explanation of the correction term of the Balmer formula through magnetic influences as proposed by Dr. Stanley Allen, it seems that we shall have to seek another explanation for these deviations.

Christiania, Feb. 8, 1915.

LXX. *On the Electron Theory of the Optical Properties of Metals.*—I. *By* G. H. LIVENS [*].

1. *INTRODUCTION.*—The explanation of the phenomena associated with electrical conduction in metals based on the electron theory, originated by Drude and Lorentz [†], was generalized for application to rapidly alternating fields such as those associated with radiation first by J. J. Thomson [‡], and then subsequently in greater detail by Jeans [§] and H. A. Wilson [||]. The general method of attack adopted by the last two authors differs essentially from the more direct methods employed by Drude and Lorentz and in the hands of Wilson, who alone works it right through on the statistical basis, it leads to formulæ which differ essentially from those obtained by Lorentz, whose results, in the opinion of the present writer, represent the only complete formulæ to be obtained from the theory as usually specified. In a recent paper on the electron theory of metallic conduction, exception was taken to the deductions of the formula for the electrical conductivity put forward by Thomson and Wilson. A correction of considerable importance was made in Wilson's detailed analysis which renders the final formula to be obtained from it more consistent with Lorentz's original results. In the present paper it was intended to carry out a promise given in my former paper and to extend this same

correction throughout the whole analysis for the optical
properties of metals along the lines laid down by Wilson
and Jeans ; but on attempting the problem along these lines
I found that the fundamental differential equation on which
the theory is constructed turned out to be identical with the
equation used by Lorentz to determine the velocity distri-
bution function. It was therefore preferred to adopt the
more direct method of attack constructed on the basis of
certain remarks bearing on this subject in a former paper *, in
order to exhibit clearly the very general validity of the method.

In addition, the opportunity will be taken to introduce a
modification of an entirely different character into the general
theory, which has long been considered necessary in a proper
treatment of the subject but which has, as far as I am aware,
never yet been introduced.

2. *General basis of the theory.*—We shall for the present
assume, with all previous writers on this subject, that the
whole of the electrical and optical properties of any metal
arise from the fact that there are a large number of electrons
in the metal free to move about in the space between the
atoms. The atoms and electrons will be presumed to be
perfectly elastic spheres, at least so far as concerns their
interaction in collision : we shall also presume that the
atoms are comparatively of such large mass that the magni-
tude and direction of the velocity of any atom and the
magnitude of the velocity of the electron are unaffected by
a collision between the two.

In the absence of any external field the atoms and elec-
trons will be moving about in a perfectly irregular manner,
and the velocity distribution will thus be exactly that
specified by Maxwell's law, so that if N is the number of
free electrons per cubic centimetre of the metal, then the
number in the same volume with their velocity components
between (ξ, η, ζ) $(\xi+d\xi, \eta+d\eta, \zeta+d\zeta)$ is given by

$$\delta N = N \sqrt{\frac{q^3}{\pi^3}} e^{qu^2} d\xi d\eta d\zeta,$$

wherein we have used

$$u^2 \equiv \xi^2 + \eta^2 + \zeta^2$$

and q for a constant connected with the mean value u_m^2 of u^2
for all the electrons by the relation

$$q = \frac{3}{2u_m^2}.$$

* "On the Electron Theory of Metallic Conduction," Phil. Mag.
March 1915.

When an electric field (of intensity E) is applied in any direction all this alters; the electrons will be pulled about by the field in such a way that they will acquire momentum at a rate of eE parallel to the direction of E. We shall assume, however, that each collision between an electron and an atom completely removes all effects imparted by the electric field during the previous free motion, so that the law of distribution of the initial velocities for the free paths being pursued at any instant will be precisely that given as above by Maxwell's law. It seems necessary to make some such assumption as this in order to ensure, for instance, the possibility of the existence of a steady state when the electric force is uniform and constant in time; and the present one is probably the most general assumption we can make* as it involves no detailed specification as to the dynamical nature of the collisions, and also enjoys the comparatively wide range of generality possessed by Maxwell's law itself.

It is assumed that collisions between electrons are too infrequent to be of any importance in the theory: this appears to be a legitimate assumption on account of the extreme smallness of the size of an electron. We shall also assume for the present, that the motion of any charged atoms is unaltered by the field, so that there will be no contribution to the current on this account.

3. *The instantaneous velocity distribution when the electric field is in action.*—On the basis of the assumptions mentioned in the last paragraph, it is possible to calculate the actual instantaneous distribution of velocities at any instant when the electrons are subject to the action of an electric force E, which will be presumed to be applied parallel to the x-axis of coordinates chosen for the analyses. In fact the number of electrons which started their paths with velocity components between (ξ_0, η_0, ζ_0) and $(\xi_0 + d\xi_0, \eta_0 + d\eta_0, \zeta_0 + d\zeta_0)$ at times which lie in the small interval between $t = \tau$ and $t = (\tau + d\tau)$ previous to the instant t is

$$\delta N_\tau = \delta N_0 e^{-\frac{\tau}{\tau_m}} \frac{d\tau}{\tau_m} \dagger,$$

where

$$\delta N_0 = N \sqrt{\frac{q^3}{\pi^3}} e^{-qu_0^2} d\xi_0 d\eta_0 d\zeta_0,$$

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* [April 1st, 1915.] It is, as a matter of fact, involved in the assumption of hard elastic spheres for both atoms and electrons.

† *Vide* Lorentz, 'The Theory of Electrons,' p. 308.

where also
$$u_0^2 = \xi_0^2 + \eta_0^2 + \zeta_0^2$$

and τ_m is the mean value of τ for all the δN_0 electrons and which is identical with the mean time between two encounters for an electron with velocity u_0.

The velocities of these electrons at the instant t are given by
$$\xi = \xi_0 + \frac{e}{m}\int_{t'=t-\tau}^{t'=t} E\,dt', \qquad \eta = \eta_0, \qquad \zeta = \zeta_0 ;$$

where t' is used as an auxiliary time variable for the integration. We write the first of these equations in the form
$$\xi = \xi_0 + \frac{e\phi}{m},$$

so that
$$\phi = \int_{t'=t-\tau}^{t'=t} E\,dt'.$$

Thus if we interpret the function δN_τ in terms of (ξ, η, ζ) instead of (ξ_0, η_0, ζ_0), we find that the number of electrons at the instant t with their velocity components between (ξ, η, ζ) and $(\xi + d\xi, \eta + d\eta, \zeta + d\zeta)$ and for which the value of τ is as specified

$$\delta N_\tau = \frac{N}{\tau_m}\sqrt{\frac{q^3}{\pi^3}}\,e^{-q\left(u^2 - \frac{2e\xi\phi}{m}\right) - \frac{\tau}{\tau_m}}\,d\xi\,d\eta\,d\zeta\,d\tau,$$

wherein we have neglected squares of the small quantity ϕ, as is usually done in these theories, and used
$$u^2 = \xi^2 + \eta^2 + \zeta^2.$$

To the same order of approximation we may also write

$$\delta N_\tau = \frac{N}{\tau_m}\sqrt{\frac{q^3}{\pi^3}}\,e^{-qu^2 - \frac{\tau}{\tau_m}}\left(1 + \frac{2qe\xi\phi}{m}\right)d\xi\,d\eta\,d\zeta\,d\tau.$$

On integration over all values of τ from 0 to ∞ we find the total number of electrons per unit volume at the instant t with their velocity components between (ξ, η, ζ) and $(\xi + d\xi, \eta + d\eta, \zeta + d\zeta)$ in the form

$$\delta N = N\sqrt{\frac{q^3}{\pi^3}}\,e^{-qu^2}\left(1 + \frac{2qe\xi}{m}\int_0^\infty \phi\,e^{-\frac{\tau}{\tau_m}}\frac{d\tau}{\tau_m}\right)d\xi\,d\eta\,d\zeta$$

$$= N\sqrt{\frac{q^3}{\pi^3}}\,e^{-qu^2}\left[1 + \frac{2qe\xi}{m}\int_0^\infty e^{-\frac{\tau}{\tau_m}}\frac{d\tau}{\tau_m}\int_{t'=t-\tau}^{t'=t} E\,dt'\right]d\xi\,d\eta\,d\zeta,$$

which is the generalized form of a result already given for two special cases of limited applicability.

If E is constant for a time large compared with the mean time between two collisions, this reduces at once to

$$\delta N = N \sqrt{\frac{q^3}{\pi^3}} e^{-qu^2} \left[1 + \frac{2qe\xi E}{m} \int_0^\infty \frac{\tau e^{-\frac{\tau}{\tau_m}} d\tau}{\tau_m} \right]$$

$$= N \sqrt{\frac{q^3}{\pi^3}} e^{-qu^2} \left[1 + \frac{2qe E \xi \tau_m}{m} \right],$$

wherein, if we write, what is approximately true,

$$\tau_m = \frac{l_m}{r},$$

we recognize Lorentz's well-known general law of distribution of velocities of the electrons under the action of a steady field.

If we put again, in a simple harmonic field,

$$E = E_0 e^{ipt},$$

we get

$$\delta N = N \sqrt{\frac{q^3}{\pi^3}} e^{-qr^2} \left[1 + \frac{2qe\xi E_0}{m} \int_0^\infty \left(\frac{e^{ipt} - e^{ip(t-\tau)}}{ip} \right) e^{-\frac{\tau}{\tau_m}} \frac{d\tau}{\tau_m} \right] d\xi d\eta d\zeta$$

$$= N \sqrt{\frac{q^3}{\pi^3}} e^{-qr^2} \left[1 + \frac{2qe\xi E_0}{m} \left(e^{ipt} - \frac{e^{ipt}}{1+ip\tau_m} \right) \right] d\xi d\eta d\zeta$$

$$= N \sqrt{\frac{q^3}{\pi^3}} e^{-qr^2} \left[1 + \frac{2qe\xi\tau_m}{m} \frac{E_0 e^{ipt}}{1+ip\tau_m} \right] d\xi d\eta d\zeta,$$

which agrees with a result obtained directly in another paper.

It appears, however, on due consideration that this last result is restricted for application to problems in which the field is represented by a simple harmonic train of *stationary* waves in which the wave-length is very long compared with the mean free path of an electron. To remove this restriction we must take account of the change of phase in the vibrations of the field from point to point in the metal, and to do this we must introduce a more general type of field. We may assume quite generally that the field is propagated in the direction of the z-axis as a plane simple harmonic wave-train

with the velocity $\frac{c}{n}$ *, so that the electric force E, which is

* *c* is the velocity of radiation in vacuo.

presumed to be polarized parallel to the x-axis of coordinates, depends on the coordinates of time and space by the exponential factor $e^{ip\left(t - \frac{n\zeta}{c}\right)}$ so that

$$E = E_0 \, e^{ip\left(t - \frac{n\zeta}{c}\right)}.$$

If we now confine our attention to all the electrons which at time t lie in or at least infinitely near the plane $z=z$ (say between $z=z$ and $z=z+dz$), then we shall have for any one of them which has been moving for a time τ since its last collision previous to the instant t

$$\phi = \frac{E_0 e^{ip\left(t - \frac{n\zeta}{c}\right)}}{ip\left(1 - \frac{n\zeta}{c}\right)} \left[1 - e^{-ip\tau\left(1 - \frac{n\zeta}{c}\right)}\right],$$

wherein (ξ, η, ζ) are used as usual to denote the velocity components of the electron at time t.

Thus the distribution of velocities among these electrons near the plane $z=z$ is such that there is at the instant t, the number

$$\delta N = N \sqrt{\frac{q^3}{\pi^3}} e^{-qu^2} \left[1 + \frac{2qe\xi E}{mip(1 - n\zeta)} \int_0^{\infty} \left(1 - e^{-ip\tau(1 - n\zeta)}\right) e^{-\frac{\tau}{\tau_m}} \frac{d\tau}{\tau_m}\right] d\xi\, d\eta\, d\zeta$$

per unit volume with their velocity components between (ξ, η, ζ) and $(\xi+d\xi, \eta+d\eta, \zeta+d\zeta)$. This gives

$$\delta N = N \sqrt{\frac{q^3}{\pi^3}} e^{-qu^2} \left[1 + \frac{2qe\xi E\tau_m}{m\left[1 + ip(1 - n\zeta)\tau_m\right]}\right] d\xi\, d\eta\, d\zeta,$$

which determines completely the velocity distribution among the electrons in and near the plane $z=z$. This is the result which will be of greatest use to us for our future work : it might easily have been obtained directly from the previous result for stationary waves by a simple application of Doppler's principle.

It must be insisted that the various formulæ here obtained are of very general application, in no way less general than Maxwell's law itself. The final results involve no assumptions as to the rapidity or otherwise of the variation in the field E, and will in fact be generally applicable for the most rapidly alternating fields. It is interesting, however, to notice that for these very rapid alternations the velocity distribution is

practically identical with that given by Maxwell's original law, which is just what we should expect, as in such circumstances the alternations of the field are too rapid to take effective hold on the inertia of the electrons.

4. *The expression for the current density.*—We are now in a position to calculate the conduction current density under the assumptions we have specified above. This is done exactly along the lines laid down by Lorentz, and is therefore given by its components (I_x, I_y, I_z) parallel to the coordinate axes, where

$$I_x = e \int \xi \delta N, \quad I_y = e \int \eta \delta N, \quad I_z = e \int \zeta \delta N$$

the integrals being extended over all values of (ξ, η, ζ) for all the electrons per unit volume.

On inserting the value of δN we find that this gives

$$I_x = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \left[\frac{2qe^2 N \xi^2}{m} \sqrt{\frac{q^3}{\pi^3}} e^{-qu^2} \int_0^\infty e^{-\frac{\tau}{\tau_m}} \frac{d\tau}{\tau_m} \int_{t'=t-\tau}^{t'=\tau} E dt' \right] d\xi d\eta d\zeta$$

$$= \frac{2Ne^2 q}{m} \sqrt{\frac{q^3}{\pi^3}} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \left[\xi^2 e^{-qu^2} \int_0^\infty e^{-\frac{\tau}{\tau_m}} \frac{d\tau}{\tau_m} \int_{t'=t-\tau}^{t'=\tau} E dt' \right] d\xi d\eta d\zeta$$

while $I_y = I_z = 0$.

This gives us the general formula for the current at time t. Particular cases are worth noticing.

(i.) If E is constant for a time large compared with the mean time between two collisions, then we have at once

$$I_x = \frac{2Ne^2 q}{m} \sqrt{\frac{q^3}{\pi^3}} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \xi^2 e^{-qu^2} \int_0^\infty E e^{-\frac{\tau}{\tau_m}} \tau \frac{d\tau}{\tau} d\xi d\eta d\zeta$$

$$= \frac{2Ne^2 q}{m} \sqrt{\frac{q^3}{\pi^3}} E \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \xi^2 \tau_m e^{-qu^2} d\xi d\eta d\zeta.$$

Now noticing that we can put, as a good approximation,

$$\tau_m = \frac{l_m}{r},$$

we see that we can at once transform the triple integral with respect to (ξ, η, ζ) by a spherical polar transformation into a single integral with respect to u from 0 to infinity, if we put

$$d\xi d\eta d\zeta = 4\pi u^2 du \quad \text{and} \quad \xi^2 = \frac{u^2}{3},$$

and we thus get

$$I_x = \frac{8\pi N e^2 q l_m}{3m} \sqrt{\frac{q^3}{\pi^3}} \, E \int_0^\infty u^3 e^{-qu^2} du \, ;$$

and using $v = qu^2$ this reduces to

$$I_x = \frac{4\pi N e^2 l_m}{3mq} \sqrt{\frac{q^3}{\pi^3}} \, E \int_0^\infty v e^{-v} dv,$$

$$= \left(\frac{4N e^2 l_m}{3m} \sqrt{\frac{q}{\pi}} \right) E,$$

which is Lorentz's result for steady currents.

(ii.) Again in the case of stationary waves of period p and comparatively long wave-length, we may use

$$E = E_0 e^{ipt},$$

and then we deduce as above

$$I_x = \frac{8\pi N e^2 q l_m}{3m} \sqrt{\frac{q^3}{\pi^3}} E_0 e^{ipt} \int_0^\infty \frac{u^3 e^{-qu^2} du}{1 + \dfrac{ipl_m}{u}}$$

which agrees with the results of my former paper.

(iii.) If, however, we use the real case of progressive simple harmonic waves we must, as above, put

$$E = E_0 e^{ip\left(t - \frac{nz}{c}\right)},$$

and then we find firstly that

$$I_x = \frac{2N e^2 l_m q}{m} \sqrt{\frac{q^3}{\pi^3}} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \frac{\xi^2 e^{-qu^2}}{\left[1 + ip\left(1 - \dfrac{n\zeta}{c}\right)\tau_m\right]} \frac{d\xi d\eta d\zeta}{u}.$$

Or again by a spherical polar transformation in which

$$\xi = u \cos \theta, \quad \zeta = u \cos \theta \cos \phi,$$

the triple integral reduces to

$$\int_0^\infty e^{-qu^2} u^3 du \int_0^\pi \cos^2\theta \sin\theta \, d\theta \int^{2\pi} \frac{d\phi}{\left(1 + \dfrac{ipl_m}{u}\right) - \dfrac{ipnl_m}{c} \sin\theta \cos\phi}.$$

Now we know that

$$\int_0^{2\pi} \frac{d\phi}{\left(1+\dfrac{ipl_m}{u}\right) - \dfrac{ipnl_m}{c}\sin\theta\cos\phi} = 4\int_0^{\frac{\pi}{2}} \frac{\left(1+\dfrac{ipl_m}{u}\right)d\phi}{\left(1+\dfrac{ipl_m}{u}\right)^2 + \dfrac{p^2n^2l_m^2}{c^2}\sin^2\theta\cos^2\phi}$$

which integrates by a well-known method and gives

$$\frac{2\pi\left(1+\dfrac{ipl_m}{u}\right)}{\sqrt{\left(1+\dfrac{ipl_m}{u}\right)^2\left[\left(1+\dfrac{ipl_m}{u}\right) + \dfrac{n^2p^2l_m^2}{c^2}\sin^2\theta\right]}}$$

$$= \frac{2\pi}{\sqrt{\left(1+\dfrac{ipl_m}{u}\right)^2 + \dfrac{n^2p^2l_m^2}{c^2}\sin^2\theta}}.$$

The integral with respect to θ is then

$$2\pi\int_0^\pi \frac{\cos^2\theta\sin\theta\,d\theta}{\sqrt{\left(1+\dfrac{ipl_m}{u}\right)^2 + \dfrac{p^2n^2l_m^2}{c^2}\sin^2\theta}}$$

which by the transformation

$$\frac{pnl_m}{c}\cos\theta = \sqrt{\left(1+\dfrac{ipl_m}{u}\right)^2 + \dfrac{p^2n^2l_m^2}{c^2}}\sin\psi$$

is directly evaluated in the form

$$2\pi\left[\frac{\left(1+\dfrac{ipl_m}{u}\right)^2 + \dfrac{p^2n^2l_m^2}{c^2}}{\dfrac{p^3n^3l_m^3}{c^3}}\right]\left[\sin^{-1}\left\{\frac{\dfrac{pnl_m}{c}}{\sqrt{\left(1+\dfrac{ipl_m}{u}\right)^2 + \dfrac{p^2n^2l_m^2}{c^2}}}\right\}\right.$$

$$\left. - \frac{\left(1+\dfrac{ipl_m}{u}\right)pnl_m}{\left(1+\dfrac{ipl_m}{u}\right)^2 + \dfrac{p^2n^2l_m^2}{c^2}}\right].$$

Calling this expression

$$4\pi\chi(u),$$

we have then on insertion in the last integral,

$$I_x = \left[\frac{8\pi Ne^2l_m q}{m}\sqrt{\frac{q^3}{\pi^3}}\int_0^\infty u^3\chi(u)e^{-qu^2}\,du\right]E_0e^{ip\left(t-\frac{nz}{c}\right)},$$

from which all the circumstances of the problem can be deduced, even though it is impossible to evaluate the last integral except perhaps approximately. We notice, however, that if the velocity u for the majority of the electrons is considerably less than $\dfrac{c}{n}$ the velocity of radiation in the metal, which condition is, I presume, nearly always fulfilled at all attainable temperatures, this formula reduces as a first approximation to that given above for stationary waves. The theory for stationary wave-radiation is therefore of rather a surprisingly wide generality, in spite of its more apparent restrictions. It will not, therefore, be necessary for us to examine the present case in any further detail, even if that were possible.

5. *On the fundamental differential equation of the Jeans-Wilson theory.*—Jeans, and Wilson following him, adopt rather a different mode of attack, based on a calculation of the rule of increase in the momentum of certain specified groups of electrons. Wilson's analysis is slightly the more general and detailed of the two, and I shall therefore confine my attention to his equations alone.

Wilson assumes that the number $d\mathrm{N}$ of free electrons per unit volume with their resultant velocities between u and $u+du$ remains practically constant, although particular electrons are continually entering and leaving the group. He therefore attributes to each such group a definite permanent existence whose average motion under the action of an electric force may be specified by a certain differential equation which he finds to be of the form

$$\frac{d}{dt}(mw\,d\mathrm{N}) = \mathrm{E}e\,d\mathrm{N} - \beta w\,d\mathrm{N},$$

wherein w is used to denote the average velocity of the group in the direction of the applied electric force E and β is some function of u, m, and e. On integration of this expression over all the groups and using

$$\mathrm{I} = e\!\int w\,d\mathrm{N},$$

Jeans' equation for the electric current density I is obtained in the form

$$\frac{d\mathrm{I}}{dt} = \frac{\mathrm{N}e^2}{m}\mathrm{E} - \gamma\mathrm{I},$$

In the theories of Jeans and Wilson this differential

equation is fundamental, but in the opinion of the present writer it is by no means complete as it stands. The following deduction of the equation may perhaps make this point clear, If δN denote, as before, the number of electrons per cubic centimetre with their velocity component between (ξ, η, ζ) and $(\xi + d\xi, \eta + d\eta, \zeta + d\zeta)$ then the component of the momentum of this group parallel to the x-axis is $m\xi\delta N$, and if E acts in the same direction we have

$$\frac{d}{dt}(m\xi\delta N) = m\delta N \frac{d\xi}{dt} + m\xi \frac{d\delta N}{dt}.$$

Now we know that

$$m\frac{d\xi}{dt} = e\mathrm{E},$$

whilst according to Wilson the change in δN in the time dt is equal to the number of collisions which take place in this group in the time dt with the sign changed, and this is

$$d(\delta N) = -d\mathrm{N} \int_0^{dt} e^{-\frac{\tau}{\tau_m}} \frac{d\tau}{\tau_m} \, *$$

$$= -d\mathrm{N} \frac{dt}{\tau_m},$$

so that

$$\frac{d}{dt}(\delta N) = -\frac{\delta N}{\tau_m};$$

and thus using $\tau_m = \dfrac{l_m}{u}$ we have the above equation in the form

$$\frac{d}{dt}(m\xi\delta N) = e\delta N\mathrm{E} - \frac{m\xi u\delta N}{l_m},$$

and on integration over all values of (ξ, η, ζ) we reproduce the Jeans-Wilson equation given above.

But the assumption that the change in δN is due entirely to the collisions is not valid. In fact δN is itself a function of (ξ, η, ζ) and therefore changes on account of the variations in these quantities. In the present instance we ought therefore to write the momentum equation in the form

$$\frac{d}{dt}(m\xi\delta N) = e\mathrm{E}\left(\delta N + \frac{\partial}{\partial\xi}(\delta N)\right) - \frac{m\xi u\delta N}{l_m},$$

* This neglects the contribution to the momentum of the group by the electrons coming into it. This does not, however, affect the final result as on integration these terms go out by themselves.

and it is then an interesting verification of our present analysis to show that if δN is given by our previous general law, viz.,

$$\delta N = N \sqrt{\frac{\overline{q^3}}{\pi^3}} e^{-qw^2} \left[1 + \frac{2qe\xi}{m} \int_0^\infty e^{-\frac{\tau}{\tau_m}} \frac{d\tau}{\tau_m} \int_{t'=t-\tau}^{t'=t} E dt' \right] d\xi \, d\eta \, d\zeta,$$

then the equation is identically satisfied.

6. *The polarization currents and the total electric field at a point in the metal.*—It must now be remembered that in the case of most metals to be dealt with, there is usually a contribution to the total current of electricity not only as the result of the motion of the various free electrons, but also as a result of the relative displacement of the neutralizing charges in each atom, caused by the electric field pulling the opposite charges in opposite directions. This part of the current is easily calculated, as has already been explained in great detail in a previous communication on absorption in dielectric media, and turns out to be of the form

$$\frac{d\mathrm{P}}{dt},$$

where P is a vector defining what is analogous to the polarization in dielectrics and whose intensity is given by

$$\mathrm{P} = \frac{\mathrm{A}}{1 - a\mathrm{A}} \mathrm{E},$$

where

$$\mathrm{A} = \Sigma \, \frac{e^2/m}{n^2 - n_0^2 + inn_0'},$$

wherein Σ denotes a sum taken over all the electronic resonators in the atoms per unit volume for the typical one of which n_0 is the period of free vibration and mn_0' the coefficient of the damping force in its equation of motion. The constant a is a numerical constant whose value in an ideal case is $\frac{1}{3}$ and in any real case is at least of this order of magnitude.

In addition to this current there is, of course, as always, to be added the æthereal displacement or polarization current, which is measured by

$$\frac{d\mathrm{E}}{dt},$$

as in the Maxwellian theory.

Now we know that the resonance electrons in the atoms

are effective in modifying the electric field at any point inside the metal, so that they will by such means also indirectly affect the currents of conduction. In fact, at any point in any homogeneous medium polarized to intensity P, there is an additional electric force of intensity

$$aP$$

in the direction of P, arising solely from the distribution of the immediately surrounding polarized molecules or atoms. We must therefore include this part of the electric field in the general expression for E, which therefore now becomes

$$E + aP.$$

This is the complete expression for the total electric force which is effective in driving the electric current.

7. *The electro-optical equations.*—The fundamental equations of the optical theory are the generalized Maxwell equations which, expressed in their differential form and using the Hertz-Heaviside system of units, are simply, for non-magnetic media

$$\frac{1}{C} I' = \text{Curl } H, \qquad -\frac{1}{C} \frac{dH}{dt} = \text{Curl } E,$$

wherein E, H denote as usual the electric and magnetic force vectors at any point in the field, I′ the total current density at the same point which is, inside the metal expressed by

$$I' = I + \frac{dE}{dt} + \frac{dP}{dt}.$$

Let us now examine the propagation of light in a medium where these equations are satisfied. In order to simplify the equations we adopt the standard convention and consider as previously the propagation of plane homogeneous waves taking place in the direction of the axis Oz, so that the components of E, H, and I′ involve the coordinates of space and time by the exponential factor $e^{ip\left(t - \frac{nz}{c}\right)}$, where n is in general a complex quantity, a function of p, the frequency of the light disturbance used.

Since in this case all differentials with respect to x and y vanish, the general equations reduce to

$$\frac{ipn}{c} H_y = \frac{1}{c} I_x', \qquad \frac{nE_x}{c} = \frac{H_y}{c},$$

and thus for the propagation of this wave-train to be possible in the medium we must have

$$ipn^2 \mathbf{E}_x = \mathbf{I}_x',$$

which is the general relation to be satisfied between the electric force and current components.

If we put

$$n = \mu - i\kappa$$

and assume that μ and κ are real the exponential factor is

$$e^{-\frac{p\kappa z}{c}} e^{ip\left(t - \frac{\mu z}{c}\right)},$$

and thus $\dfrac{c}{\mu}$ is the velocity of the disturbance in the medium, and therefore μ is the ordinary refractive index. The absorption is determined by κ, which is therefore called the absorption coefficient.

8. *The equations in the metal.*—Now we know $\mathbf{I}_x$ in terms of $\mathbf{E}_x$ and can therefore at once proceed to an examination of the equations as far as they concern the propagation in the metal itself.

If $\mathbf{E}_x$ is, as above, of the form $\mathbf{E}e^{ip\left(t - \frac{nz}{c}\right)}$ then we know that

$$\mathbf{I}_x' = \mathrm{C}(\mathbf{E}_x + a\mathbf{P}_x) + \frac{d\mathbf{E}_x}{dt} + \frac{d\mathbf{P}_x}{dt},$$

where C is used for the generalized form of the conductivity which we have found to be

$$\mathrm{C} = \frac{4\pi \mathrm{N} e^2 l_m q}{m} \sqrt{\frac{q^3}{\pi^3}} \int_0^\infty u^3 \chi(u) e^{-qu^2} du,$$

$\chi(u)$ having the same significance as before; but

$$\frac{d\mathbf{E}_x}{dt} = ip\mathbf{E}_x, \qquad \frac{d\mathbf{P}_x}{dt} = ip\mathbf{P}_x$$

and

$$\mathbf{P}_x = \frac{\mathbf{A}\mathbf{E}_x}{1 - a\mathbf{A}}$$

as before, so that

$$\mathbf{I}_x' = \left[\frac{\mathrm{C}}{1 - a\mathbf{A}} + ip\left(1 + \frac{\mathbf{A}}{1 - a\mathbf{A}}\right)\right]\mathbf{E}_x.$$

We therefore conclude that

$$n^2 = \frac{C}{ip(1-a\mathrm{A})} + 1 + \frac{\mathrm{A}}{1-a\mathrm{A}}$$

or again

$$(\mu - i\kappa)^2 = \frac{C}{ip(1-a\mathrm{A})} + \left(1 + \frac{\mathrm{A}}{1-a\mathrm{A}}\right)$$

which is the fundamental equation of the theory in its most general form.

If we write

$$(\mu_0 - i\kappa_0)^2 = 1 + \frac{\mathrm{A}}{1-\mathrm{A}a},$$

so that μ_0 and κ_0 would be the refractive index and absorption coefficient respectively of the metal if the free electrons were extracted, and if also we can separate C into real and imaginary parts in the form

$$C = C_1 + iC_2,$$

then we may conclude that

$$\mu^2 - \kappa^2 = \mu_0{}^2 - \kappa_0{}^2 + \frac{C_2}{p(1-a\mathrm{A})}, \quad *$$

whilst

$$\mu\kappa = \mu_0\kappa_0 + \frac{C_1}{p(1-a\mathrm{A})}.$$

The whole question thus turns on the determination of C and its separation into real and imaginary parts. We have above given the most general form for C obtainable on the basis of the present theory, but it is probably too complicated to be of any assistance in the present instance, and we must have resort to the first approximation furnished by the analysis for stationary waves. In fact, if the velocities of the greater majority of the electrons are considerably smaller than the velocity of propagation of radiation in the medium, we may write with a sufficient approximation even for progressive waves

$$C = \frac{8\pi Ne^2 q l_m}{3m} \sqrt{\frac{q^3}{\pi^3}} \int_0^\infty \frac{u^3 e^{-qu^2} du}{1 + \frac{ipl_m}{u}},$$

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* This separation is not correct since A is also complex; but it is probably sufficient in any real case to take A in the terms in C with its real value alone.

so that

$$C_1 = \frac{8\pi N e^2 q l_m}{3m} \sqrt{\frac{q^3}{\pi^3}} \int_0^\infty \frac{u^3 e^{-qu^2}\, du}{1 + \dfrac{p^2 l_m^2}{u^2}}$$

and

$$C_2 = -\frac{8\pi N e^2 q l_m^2 p}{3} \sqrt{\frac{q^3}{\pi^3}} \int_0^\infty \frac{u^2 e^{-qu^2}\, du}{1 + \dfrac{p^2 l_m^2}{u^2}},$$

which appear to be the most generally applicable results which it is possible to determine from the present form of theory.

It must be noticed that C_1 is the ordinary expression for the conductivity and can be written in the more usual form, if we use

$$v = qu^2,$$

$$C_1 = 2\sqrt{\frac{2}{3\pi}}\, \frac{N e^2 l_m}{m u_m} \int_0^\infty \frac{v e^{-v}\, dv}{1 + \dfrac{p^2 l_m^2 q}{v}}.$$

9. *The emission of light by the metal and the complete radiation formula.*—The emission of light by the metal as a result of the electronic motions taking place in its interior has been fully discussed by Lorentz and subsequently by Thomson, Jeans, Wilson, and others. Under the fundamental assumptions on which the present theory is based, it is found that the emissivity of a thin plate of any metal of small thickness Δ and for light of period p is

$$E' \equiv \frac{N e^2 l_m p^4}{24\, c^4 \pi^4 q} \sqrt{\frac{q}{\pi}} \int_0^\infty \frac{v e^{-v}\, dv}{1 + \dfrac{p^2 l_m^2 q}{v}},$$

the notation being exactly the same as in the present paper.

The coefficient of absorption for such a thin plate is shown by Lorentz to be equal to $\dfrac{\sigma \Delta}{c}$, where σ denotes the conductivity, so that it is

$$A' \equiv \frac{4\pi N e^2 l_m \Delta}{3 c m q} \sqrt{\frac{q^3}{\pi^3}} \int_0^\infty \frac{v e^{-v}\, dv}{1 + \dfrac{p^2 l_m^2 q}{v}},$$

so that we have, with Lorentz,

$$E_\lambda = \frac{8\pi}{c}\frac{E'}{A'} = \frac{p^4 m}{4c^4\pi^3 q},$$

or using

$$q = \frac{3}{2u_m{}^2}, \quad p = \frac{2\pi c}{\lambda},$$

we have

$$E_\lambda = \frac{8\pi m u_m{}^2}{\lambda^4}.$$

The present analysis thus verifies completely what was surmised in a former communication, viz. that Kirchhoff's law, which affirms that E_λ is independent of the particular metal under consideration, is absolutely true on the basis of the present theory. The incompatibility of the previous results rested in the formula adopted for the conductivity which has in the present instance been considerably modified.

It thus appears that the variation from the above law obtained by Wilson in his analysis is not, as he says, due to the neglect of the motion of the atoms and the mutual influence of the electrons, but rather to an incompleteness in his analytical investigation of the statistical motions of the electrons themselves.

The reason why the present form of theory fails to give an appropriate form of E_λ has been fully discussed in another place and need not detain us any longer here.

10. *On the dissipation of energy.*—Before closing this paper I think it is necessary to point out an apparent discrepancy in the present form of theory, which at first escaped my notice.

According to Thomson the energy dissipated per second in a unit volume of the metal is equal to the work done by the electric force on the electrons during the whole of their free path motions, and according to a calculation I made of this work in the case when the electric force E is given by

$$E = E_0 \cos pt,$$

I found that the energy dissipated per unit time and volume is

$$H = \sqrt{\frac{2}{3\pi}}\frac{Ne^2 l_m E_0{}^2}{mu_m}\int_0^\infty \frac{e^{-v}\,dr}{1 + \dfrac{p^2 l_m{}^2 q}{r}}, \quad *$$

which is taken to be equal to the mean value of $\sigma' E^2$, which

* Phil. Mag. January 1915.

is $\frac{1}{2}\sigma' E_0{}^2$. We thus conclude that

$$\sigma' = 2\sqrt{\frac{2}{3\pi}} \frac{Ne^2 l_m}{mu_m} \int_0^\infty \frac{e^{-v}\,dv}{1 + \dfrac{p^2 l_m{}^2 q}{v}}.$$

In the above discussion and also in a previous paper, I find, however, that the more consistent value for σ is

$$\sigma = 2\sqrt{\frac{2}{3\pi}} \frac{Ne^2 l_m}{mu_m} \int_0^\infty \frac{v e^{-v}\,dv}{1 + \dfrac{p^2 l_m{}^2 q}{v}}.$$

Wilson obtains by both of his methods formulæ which differ from the first of these by a factor $\frac{3}{2}$, but his deductions are I believe both incomplete.

There is unfortunately a mistake in my previous work which considerably affects the final formula. The result of the integration at the top of page 182 of the paper mentioned should have its denominator squared. On making this correction a formula for the conductivity is obtained which is perfectly consistent with that given above, so that there is no real discrepancy*.

11. *Conclusion.*—It thus appears that a detailed analysis of the motion of the electrons in the metal along lines suggested by Thomson and Lorentz enables us to formulate a complete theory for the action of the most rapidly alternating fields in the metal. Moreover, this theory is perfectly consistent with the special deductions given by Lorentz in the particular case of steady fields, and in this respect shows a distinct advantage over the form of theory proposed by H. A. Wilson.

A discussion of the actual bearing of the present form of theory on the fundamental question as to the number of free electrons taking part in conduction will be reserved for a future communication.

The University, Sheffield,
    Nov. 14, 1914.

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* This mistake was kindly pointed out to me by Dr. Bohr. I must also add that through the kindness of Dr. Bohr I have, since the above was written, had the pleasure of reading his Dissertation on the present subject, published in 1911. Reference will be made to this work in future papers.

LXXI. *Lead and the End Product of Thorium.* (Part II.)[*]
By Arthur Holmes, *A.R.C.S., B.Sc., F.G.S., Imperial College, London, and* Robert W. Lawson, *M.Sc., Radium Institute, Vienna* [†].

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§ 9. Constant of Disintegration of Thorium E.

THE results we have so far obtained show indirectly that thorium E is an unstable element, even though the radiation from it has not hitherto been detected. In order to obtain information as to its half-life period we must, then, resort to some method other than those usually used. The present section gives a more complete treatment of a method outlined recently by one of the authors [‡]. Before passing on to this, however, the suggestion made recently by Fajans in this connexion must be considered [§]. Using the results of an analysis by Boltwood [||] of a thorium mineral poor in uranium (thorite), and assuming that all the lead estimated had its origin in thorium, Fajans gave 2.10^7 years as the maximum possible value of the half-period of thorium E. Absence of knowledge regarding the age of the mineral referred to, renders it difficult if not impossible to determine by how much this value is too great; and in the case of another thorite analysis (by Holmes, *loc. cit.* 1911), also used by Fajans, where the age is known, it is certain that not more than 12 per cent. of the total lead found can be due to thorium. Using this fact, it can be readily shown that the Th E/Th ratio is 8.10^{-5}, from which the half-period of thorium E is found to be about $1\cdot2.10^6$ years. The thorium content of this mineral has been given in Table I. No. 3 (Part I.).

Since thorium E is unstable, it is clear that definite and reliable results for the half-period of this element can only be obtained from analyses of minerals rich in thorium. A

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[*] Part I. of this paper was published in this Magazine, vol. xxviii. pp. 823–840 (Dec. 1914).
[†] Communicated by the Authors.
[‡] Lawson, 'Nature,' July 9, 1914, p. 479.
[§] Fajans, *Heidelberger Akad. Ber.*, Abh. xi. p. 12 (1914).
[||] Boltwood, Am. Journ. Sci. xxiii. p. 88 (1907).

fortuitous choice of analyses would be useless for our purpose. The effect of thorium lead must be sufficiently predominant to exert a marked influence in spite of the unavoidable presence of uranium lead. Moreover, it cannot be lightly assumed that in all the minerals given in the above mentioned table, the amount of original lead is the same; and in the event of thorium lead being of relatively short life, it is clear that negligence of this inequality would lead to indefinite or even conflicting conclusions regarding the half-period of thorium E.

Careful consideration of the analyses made it clear that the only results which could be used with confidence were those of Nos. 3, 6, 7, and 12. The instability of thorium lead, and the large percentage of uranium in mineral No. 12, makes it certain that the effect of thorium E in affecting the Pb/U ratio of this mineral must be very small and, practically speaking, negligible. The value ($0 \cdot 041$) for this mineral can thus be taken with great probability as representative of Devonian minerals. Also, since these four minerals are similar in type, comparable in composition, and from the same locality, it is possible that their contents of original lead are not very different. Vogt [*] has given $0 \cdot 000x$ gram as the average amount of lead in 100 grams of rock. If we assume this value, and give x the value 5, the corrected Pb/U ratios for those minerals poor in thorium show a better agreement than previously. Complete agreement is not to be expected from what has already been said, but the magnitude of this value is evidently of the right order. The value $0 \cdot 0005$ gram will thus be taken as the amount of original lead in 100 grms. of the minerals used for the calculation of the half-period of thorium E by the first two of the following three methods to be described.

The total amount of experimentally found lead is evidently equal to the sum of the following three constituents :—
(*a*) Original lead ; (*b*) Uranium lead ; (*c*) Thorium lead. This statement can obviously be expressed in the following form—

$$\mathrm{Pb}_t = \mathrm{Pb}_o + k \cdot \mathrm{U}_t + m \cdot \mathrm{Th}_t,$$

where Pb_t, U_t, and Th_t are the present percentage contents of the minerals in lead, uranium, and thorium respectively. Pb_o is the quantity of original lead present per 100 grams of the mineral ; k is the amount (constant) of uranium lead associated with one gram of uranium in these Devonian minerals ; and m is the equilibrium amount of thorium lead associated with one gram of thorium.

(*a*) In the first method for the determination of the value

* Vogt, *Zeit. für prakt. Geol.* 1898 ; Holmes, *loc. cit.* p. 253.

of m, the amount of original lead is assumed as above, and the values of k and m are obtained by solution of two equations obtained as follows. The results of any two of the four analyses Nos. 3, 6, 7, 12 are substituted in the above equation, and the two equations obtained by different combinations of the analyses give on solution the required values of k and m. In the following table is given the series of results so obtained:—

TABLE VI. *a.*

Combination of Analyses.	Value of k.	Value of m.
Nos. 3 : 6	0·043	$5 . 10^{-5}$
„ 3 : 7	0·044	$4 . 10^{-5}$
„ 3 : 12	0·042	$7 . 10^{-5}$
„ 6 : 7	0·045	$1 . 10^{-5}$
„ 6 : 12	0·042	$8 . 10^{-5}$
„ 7 : 12	0·042	$8 . 10$

Mean $= 6 . 10^{-5}$

The value obtained from 6 : 7 is undoubtedly too low, and is due to these two analyses being almost alike.

(*b*) In the second method we assume $Pb_o = 0·0005$, and the value of k to be $0·042$ for Devonian minerals, and find the value of m from each of the four analyses Nos. 3, 6, 7, and 12. Before passing on, there is one point to be mentioned in connexion with the value of k above stated. The Pb_t/U_m ratio for No. 12 expressed in terms of the time-average value of uranium is $0·041$. In this discussion the actual amount of uranium present is being used in the calculations, and hence we must use the ratio between the present lead and uranium contents of the minerals Pb/U. For mineral No. 12 this is equal to $0·042$. As in the previous case, we require the equation $Pb_t = Pb_o + k . U_t + m . Th_t$ for the purpose of calculating m, which is the only unknown present. The following table gives the results obtained by this method:—

TABLE VI. *b.*

No. of Analysis...	3.	6.	7.
Value of m	$7 . 10^{-5}$	$10 . 10^{-5}$	$9 . 10^{-5}$

Mean $= 8·7 . 10^{-5}$

There is as good an agreement between this mean and that found by the previous method, as was to be expected from the value of the lead-uranium ratio there found.

(*c*) The value of *m* can also be calculated from the four analyses already used, and without any assumption as to the distribution of lead. The unknowns in the expression $Pb_t = Pb_o + k \cdot U_t + m \cdot Th_t$ are clearly Pb_o, *k*, and *m*. By insertion of the results of three of the chosen analyses, three equations are obtained which can be solved for the unknown terms. From the four sets of three equations obtained by use of the analyses 3, 6, 7, 12, the values of *m* given in the following table were obtained. The mean value of $m = 7.10^{-5}$ here obtained is practically the mean of those obtained by the two preceding methods, and corresponds to a half-period for thorium E of $7.10^{-5} \times 1.5 \cdot 10^{-10} = 1.05 \cdot 10^{6}$ years. It is interesting to note that the present method is quite independent of the stability or instability of thorium E. Moreover, since the lead producing power of thorium is only 0·4 that of uranium, it follows that, were thorium E a stable isotope of lead the value of *m* would be $0.4 \times 0.042 = 0.017$, instead of 7.10^{-5} as found (0·042 being the uncorrected lead-uranium ratio for minerals of Devonian age). The wide difference between these two values of *m* leaves little doubt that thorium E is relatively unstable. With the object of fixing the value of the half-period of thorium E more definitely, it is the intention of the authors to examine other suitable minerals of different ages, and to apply to these the same method for the evaluation of the half-period. That the results for the unknowns given in Table VI. *c* differ from

TABLE VI. *c*.

Combination of Analyses.	Value of Pb_o.	Value of *k*.	Value of *m*.
Nos. 3, 6, 7	0·0010	0·044	2.10^{-5}
„ 3, 7, 12	0·0000	0·042	$11.4 \cdot 10^{-5}$
„ 3, 6, 12	0·0001	0·042	10.10^{-5}
„ 6, 7, 12	0·0026	0·042	$5 \cdot 10^{-5}$

Mean$= 7.1 \cdot 10^{-5}$

the mean more than in the other cases is only to be expected, since any slight error in the values of the substitutes will most probably be magnified during the process of solution

of the equations. Our previous assumption regarding the magnitude of k is confirmed. The mean value of $Pb_o = 0\cdot0009$ is not far removed from that assumed in the first two methods. The result $0\cdot0026$ obtained from Nos. 6, 7, 12 is certainly too high, the reason most likely being that the analyses 6 and 7 are practically the same.

§ 10. Bismuth as a Possible End Product of the Thorium Series.

The results obtained in the present section have an important significance in relation to another possible end product of thorium. Were thorium E, with a half-period of about 10^6 years, to emit α rays, these should, according to the Geiger-Nuttall law, have a range of about 3 cm. This fact renders it highly improbable that we have here to do with an α-ray product, because α rays with the above range would hardly have escaped detection. This would appear to exclude the possibility of the end product being an isotope of mercury in Group II. b of the Periodic Classification. It seems more likely that the disintegration of thorium E is accompanied by the loss of a β ray, which would bring the resulting product into the position of bismuth in Group V. b. In such a case, we are again faced with the task of deciding whether what we may by analogy call thorium-bismuth is a stable or an unstable product. Here again the method used in the present section might be applied. A systematic examination of thorium minerals for bismuth and thorium would be necessary. If the end product of thorium is a stable bismuth isotope, the ratio Bi/Th for minerals of the same age should be constant, whereas for minerals of different ages it should vary in a similar manner to that found in the case of the Pb/U ratio. On the other hand, if the Group V. b product of thorium is unstable, the suggested analyses would serve to determine its disintegration constant. The following expression would be used in this connexion—$Bi_t = Bi_o + n \cdot Th_t$. Insertion of the results of two suitable analyses would result in two equations from which the amount of original bismuth (Bi_o) and the equilibrium constant (n) between thorium-bismuth (thorium F) and thorium could be found. From the value of n so obtained, the half-period of thorium F could be calculated, and evidence adduced as to whether the succeeding change takes place with loss of an α ray or of a β ray. In the former case, the succeeding product would be an isotope of thallium with atomic weight $204\cdot4$ (Group III.b), and in the latter an isotope of polonium (Group VI. b).

Hofmann [*] has given the results of his analyses of two samples of Bröggerite, from which the following percentage constituents have been calculated. It is clear that if the end

TABLE VII.

Sample.	U.	Pb.	Th.	Bi.	U_m.	Th_m.	Age of mineral in millions of years,	
							from Pb/U_m ratio [1].	from Bi/Th_m ratio.
I.......	67·40	8·61	4·10	0·30	72·35	4·27	1000	1490
II.......	67·08	8·49	4·63	0·33	71·96	4·82	990	1440

[1] The lead ratios agree with those of the minerals given in Table II. Part I. p. 835, Moss district, Norway, Age pre-Jatulian.

product of the thorium series is a stable isotope of bismuth [†], we may use the Bi/Th_m ratio to determine the age of the mineral. Moreover, the age as calculated in this manner should agree with that as found from the Pb/U_m [‡] ratio. The two expressions for the age of the mineral will be respectively $Bi_t/Th_m \times 2 \cdot 09 \cdot 10^{10}$ years, and $Pb_t/U_m \times 8 \cdot 58 \cdot 10^9$ years. Th^m and U_m are the respective time-average values of the thorium and the uranium contents of the mineral, and the ages as found in the case of the mineral under consideration are given in the last two columns of Table VII. In consideration of the relatively small percentages of thorium and bismuth present, and the difficulty of their estimation, it might be thought that the agreement between the ages were sufficiently satisfactory to favour the view that thorium-bismuth ("thorium F") might be a *stable* product.

Opposed to this view, however, is the fact that in the collection of analyses of thorite and allied minerals cited by Hintz in his 'Mineralogie,' vol. i. p. 1675, there is not a single determination of bismuth. Moreover, the Devonian minerals already examined by us have been tested for bismuth with negative results. Hillebrand (Bull. 220, p. 114, U.S.G.S., 1903) gives two analyses of uraninite which

[*] Hofmann, *Ber. d. d. Chem. Ges.* xxxiv. p. 914 (1901).

[†] The part played by original bismuth in such minerals is almost certainly quite negligible. For instance, Vogt (*loc. cit.*) suggests $0 \cdot 00000 x$ grm. as the average amount of bismuth in 100 grams of rock (*cf.* Holmes, *loc. cit.* 1911, p. 253).

[‡] If actinium lead is unstable, the results obtained for the age of a mineral from the Pb/U ratio will be rather low, and if the end product of actinium is bismuth, the age obtained from the Bi/Th ratio will be slightly high.

include determinations of bismuth, but the latter is clearly independent of the thorium present in each case. More recently Soddy[*] has examined Ceylon thorite for bismuth and has failed to find an appreciable amount. The evidence is thus fatal to the view that an isotope of bismuth might be the end product of the thorium series.

§ 11. Further Evidence from Atomic Weight Estimations.

An initial objection to the view that the end product of the uranium family is lead, was that the theoretical atomic weight of the end product radium G did not agree with the atomic weight of lead ($207 \cdot 1$) as closely as could be desired. The recent discovery of isotopic series of elements has demonstrated that chemical identity does not necessarily imply equivalence of atomic weight, and the objection has now lost its original force. Radium G ought to have an atomic weight of $206 \cdot 2$, calculated from the atomic weight of uranium ($238 \cdot 2$) [†], or $206 \cdot 0$ if calculated from the atomic weight of radium ($226 \cdot 0$) [‡]. The difference between these two values is very small when we consider the intrinsic difficulties of the atomic weight determinations; and the results bear excellent testimony to the careful and exact atomic weight determinations of Hönigschmid. Fortunately, a number of determinations of the atomic weight of lead extracted from radioactive minerals is already to hand, and the results are very gratifying. Thanks to the energy with which investigators are attacking the problem, the amount of evidence of this nature will soon be considerable, so that further conclusions with regard to the lead disintegration products and their stability will be possible. We may now take the theoretical value for the atomic weight of radium G to be $206 \cdot 2$ without appreciable error. Quite recently Hönigschmid and Fräulein St. Horovitz [§], Richards and Lembert[||], and Maurice Curie[¶], have published the results of their experiments in this connexion. Hönigschmid and Frln. St. Horovitz determined the atomic weight of lead

[*] *Nature*, vol. xciv. Feb. 4th, 1915, p. 615.

[†] Hönigschmid, *Wien. Anz.* 22nd January, 1914.

[‡] Hönigschmid, *Wien. Sitzungsber.* cxx. p. 1617 (1911); cxxi. p. 1973 (1912); cxxi. p. 2119 (1912).

[§] Hönigschmid and St. Horovitz, *Wien. Anz.* 12th June, 1914; *Zeit. für Elektroch.* xx. p. 319 (1914); *C. R.* clviii. p. 1797 (1914).

[||] Richards and Lembert, Journ. Am. Chem. Soc. vol. xxxvi. 7. p. 1329 (1914); *Zeit. für Anorg. Chem.* lxxxviii. p. 429 (1914). See also Fajans, *Heid. Akad. Ber.* A. Abh. xi. (1914).

[¶] Maurice Curie, *Comptes Rendus*, clviii. p. 1676 (1914).

extracted from the Joachimstal (Bohemia) uranium residues, and found the value to be $206 \cdot 736 \pm 0 \cdot 009$. Richards and Lembert used lead chloride which had been obtained by working up (*a*) North Carolina uraninite, (*b*) Joachimstal pitchblende, (*c*) Colorado carnotite, (*d*) Cornwall pitchblende, and obtained the following values respectively:— $206 \cdot 4$, $206 \cdot 57$, $206 \cdot 59$, and $206 \cdot 86$. The result for (*a*) is of particular interest, because uraninite is less likely to contain ordinary lead than pitchblende, which is a secondary form of uraninite, and in which ordinary lead may probably be present as impurity. The Joachimstal pitchblende is non-crystalline in structure, and generally contains within its mass veins of other minerals such as galena, and iron and copper pyrites. The uranium residues, obtained from large quantities of the ore, would thus be expected to have a larger content in ordinary lead than selected samples of the pitchblende. This fact is probably the cause of the difference in the atomic weights $206 \cdot 74$ and $206 \cdot 57$ obtained for lead from Joachimstal pitchblende by Hönigschmid and St. Horovitz on the one hand, and by Richards and Lembert on the other. For lead which had been extracted from carefully selected samples of pitchblende free from galena, the former experimenters obtained an atomic weight $206 \cdot 40$ *. For ordinary lead treated by the same method as their other materials, Richards and Lembert obtained the value $207 \cdot 15 \pm 0 \cdot 01$, a figure in close agreement with that given in the International Table. The preliminary results given by M. Curie vary between $206 \cdot 36$ and $206 \cdot 64$ for uranium minerals, whilst for ordinary lead from galena he found the value $207 \cdot 01$.

The results so far obtained clearly show that the lead extracted from uranium minerals (in all the above minerals the quantity of thorium present was very small) has a lower atomic weight than ordinary lead, though the value is higher than is to be expected from theory. It is quite possible that the discrepancy is due to the presence of ordinary lead in the minerals used, as well as to the presence of actinium lead, of which the atomic weight is considered by Fajans † to be about 207, and by other workers as high as 210. The presence of one or both of these elements would give an increased atomic weight in the right direction, and so at least in part explain the discrepancy.

Still more recently Hönigschmid and Fräulein St. Horovitz‡ have determined the atomic weight of the lead extracted from (*a*) Uraninite from Morogoro in German East Africa, and

* Hönigschmid and St. Horovitz, *Wien. Anz.* 9th July, 1914.
† Fajans, *loc. cit.* p. 11 (1914).
‡ Hönigschmid and St. Horovitz, *Wien. Anz.* 15th October, 1914.

(b) Bröggerite from Norway.   In the first case they obtained a mean value 206·04, and in the second case 206·06.   These results would appear to indicate that the presence of ordinary lead as impurity was responsible for the high results obtained with other minerals.   The purity of the first mineral (a), and the fact that the second mineral (b) is an old primary unaltered mineral, lend support to the view that these contained a minimum quantity of ordinary lead.   The above results show that the lead extracted from the minerals mentioned was practically pure radium G.

In the case of thorium lead the evidence is as yet less clear than in the case of uranium lead.   If we assume the atomic weight of thorium to be 232·4, then the atomic weight of thorium lead, derived by loss of six helium atoms from thorium, is to be expected to be 208·4 *.   Soddy and Hyman † have extracted lead from thorite (Ceylon), and in the two preliminary determinations of the atomic weight they have already published, they arrived at the values 208·3 and 208·5.   From the known rates of disintegration of uranium and thorium, it can readily be seen from the analysis of the mineral used by the authors cited, that if all the lead were of radioactive origin and thorium lead stable, there should be about thirteen times as much thorium lead present as uranium lead.   The theoretical atomic weight to be expected can thus be shown to be 208·24, a result less than that found experimentally.   Unfortunately, the evidence in the present case must still be regarded as inconclusive. Richards and Lembert (*loc. cit.*) have determined the atomic weight of lead separated from thorianite from Ceylon.   This material contained 60 per cent. thorium and 20 per cent. uranium, so that if thorium lead be stable, the atomic weight to be expected would be 207·40.   The value they actually obtained was 206·82, suggesting at once the instability of thorium lead.   That this result is higher than those found for the other minerals they used, cannot without further evidence be assumed to be due to the presence of a stable thorium lead.   The presence of ordinary lead as an original constituent of the mineral, or as an infiltrated secondary product, would very well explain the difference.   M. Curie obtained for lead extracted from monazite sand the value 207·08.   Here again we are not certain of the rôle played by ordinary lead, and furthermore, this mineral always contains a certain quantity of uranium which would introduce a disturbing factor owing to the presence of radium G.

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* If the atomic weight of thorium is 232·2, as determined by Hönigschmid (1914), then that of thorium lead would be 208·2.

† Soddy & Hyman, Trans. Chem. Soc. cv. 1914, p. 1402.

From the evidence of atomic weights, we can safely decide that the existence of uranium lead with a lower atomic weight than that of ordinary lead has been proved. Moreover, the most recent results of Hönigschmid show that this has an atomic weight in almost perfect agreement with that theoretically to be expected. In the case of thorium lead the evidence is much less certain, a fact undoubtedly following from the instability of thorium lead (thorium E).

The following table summarizes the evidence from atomic weights up to the present time.

TABLE VIII.*
Atomic Weights of Lead from Radioactive Minerals.

Type of Lead.	Experimenter.	Source of material.	Expected results.[1]	Actual results.
Ordinary lead.	Hönigschmid.	....	207·1[2]	207·18
,, ,,	Richards and Lembert.	....	207·1	207·15
,, ,,	M. Curie.	Galena.	207·1	207·01
Uranium lead.	Hönigschmid and St. Horovitz.	Uranium residues (Joachimstal).	>206·2	206·74
,, ,,	,,	Selected pitchblende (Joachimstal).	>206·2	206·40
,, ,,	,,	Uraninite.[3] (G. E. Africa).	206·2	206·04
,, ,,	,,	Bröggerite (Norway).[4]	206·2	206·06
,, ,,	Richards and Lembert.	Uraninite (North Carolina).	206·2	206·40
,, ,,	,,	Pitchblende (Joachimstal).	>206·2	206·57
,, ,,	,,	Carnotite (Colorado).	>206·2	206·59
,, ,,	,,	Pitchblende (Cornwall).	>206·2	206·86
,, ,,	Maurice Curie.	Pitchblende.	>206·2	206·64
,, ,,	,,	Carnotite.	>206·2	206·36
,, ,,	,,	Yttrio-tantalite.	>206·2	206·34
Thorium lead.[5]	Soddy & Hyman.	Thorite (Ceylon).	208·24	208·40
Thorium lead + Uranium lead.	Richards and Lembert.	Thorianite (Ceylon).	207·40	206·83
,, ,,	Maurice Curie.	Monazite sand.	?	207·08

[1] If thorium E and radium G are isotopic with lead, and are the respective stable end products of the thorium and uranium families of radio-elements.

[2] International atomic weight.

[3] Marckwald, *Centralblatt für Min. u. Geol.* 1906, p. 761; *Chemisches Centralblatt*, 1907, i. p. 369.

[4] This result would appear to point to the stability of thorium E, if the atomic weights of thorium E and radium G are respectively 208·4 and 206·0. Remembering, however, that in all probability a small quantity of original lead is present in this mineral, it is clear that we must be cautious in drawing conclusions regarding the stability of thorium E from such a result, where the mineral contained only 4 per cent. of thorium. Moreover, the theoretical atomic weight of radium G, 206, is likely to be a minimum value.

[5] Theoretically 90 per cent. pure.

* A revision of Table V. in Part I. p. 839.

§ 12. REMARKS ON THE SELECTION OF MATERIAL FOR
ATOMIC WEIGHT DETERMINATIONS.

If the conclusions reached in the foregoing sections are correct, we are given a reliable means of guiding the selection of material for the determination of the atomic weights of uranium lead and thorium lead respectively. It is obvious in the former case that the most suitable material is a mineral rich in uranium—such as uraninite—and practically free from thorium. In order to eliminate the effect of original lead in controlling the atomic weight of the extracted lead, it is further clear that the older the mineral, the nearer to the theoretical value 206·2 should be the value of the atomic weight actually found. Since thorium lead is relatively unstable, any effect which the presence of thorium in the mineral might exert will also be eliminated by using geologically old minerals.

The case of thorium lead, however, is not so definite. Here, clearly, rich thorium minerals with as small a percentage of uranium as possible must be used. Further, the best results will be obtained for geologically young minerals, since once the equilibrium amount of thorium lead has been formed, additional time only results in addition of more and more uranium lead, which tends to give a lower value than the theoretical value 208·4 for the atomic weight of thorium lead. The magnitude of this effect is clearly shown by the following example. Suppose we have a mineral with 60 per cent. thorium and 0·4 per cent. uranium, and that we assume it is of post-Cretaceous age, with a lead-uranium ratio of the order 0·01. On the results of the previous sections it follows that the amount of uranium lead present per 100 grams of the mineral will be $0·4 \times 0·01 = 0·0040$ gram; the amount of thorium lead present will be $60 \times 7·10^{-5} = 0·0042$ gram; and the amount of original lead $0·000x$ gram. Thus in such a case—and a thorium mineral more free from uranium will be difficult to find—the atomic weight obtained, instead of being equal to the theoretical value 208·4, would lie at about 207·2. This number is practically equal to the atomic weight of ordinary lead, so that in the present case this element would be without appreciable effect. Thus it would appear to be a difficult matter to obtain a thorium mineral which would give a higher value for the atomic weight of its contained lead than about 207, and the inevitable presence of ordinary lead in minerals prohibits exact calculation of the atomic weight of thorium lead from that found for the lead mixture.

In the case of minerals of greater age than that assumed

above—and all the minerals hitherto examined are actually very much older—the atomic weights to be expected would be somewhat lower than 207·2. It is interesting to notice that the actual determinations by Richards and Lembert on Ceylon thorianite, and by Curie on monazite, give results in complete harmony with this conclusion. This experimental verification adds still further support to the view that thorium lead is unstable.

§ 13. The Possible End Product of the Actinium Series.

When uranium is present in a mineral, actinium lead will always be a disturbing factor. Should actinium lead be a stable product, the minimum value of the atomic weight of lead extracted from a thorium-free uranium mineral would be 206·26 if the atomic weight of actinium lead is 207, and 206·50 if the atomic weight of actinium lead is 210. On the other hand, if actinium lead is of relatively short life, and if about 8 per cent. of uranium is transformed along the actinium series, then the high degree of stability of uranium lead renders it certain that the atomic weight of the latter would be quite inappreciably affected by the presence of actinium lead, even if this has an atomic weight of 210. The recent determinations of the atomic weight of lead from crystalline pitchblende and bröggerite by Hönigschmid, indicate either that the atomic weight of actinium lead is 207, or that if it is 210 then actinium lead is an unstable product. In the case that it is unstable, evidence with regard to its half-period might be obtained by determining the atomic weight of lead of radioactive origin, obtained on the one hand from geologically young, and on the other hand from geologically old, uranium minerals. It is clear that a higher value should be obtained in the former case than in the latter.

Regarding the end product of actinium there would appear to be three possibilities, each of which we will now consider in turn.

As mentioned in a previous paragraph, the atomic weight determinations of radium G by Hönigschmid indicates that if actinium lead has an atomic weight of 210, it must be unstable, otherwise instead of obtaining a value 206·04 for lead from Morogoro pitchblende, the value 206·50 should have been found. It would thus appear certain that the end product of actinium cannot be a stable lead isotope unless this has an atomic weight nearly the same as radium G.

The second possibility is that the end product is an isotope

of bismuth. There is ground for believing that if actinium lead is unstable, it will disintegrate with the loss of a β ray and the resulting formation of a bismuth isotope. As to whether or not this product is stable could readily be tested. We require the bismuth and uranium contents of a series of uranium minerals. The fact that about 8 per cent. of the uranium in a mineral disintegrates along the actinium series gives a direct means of testing whether the amount of bismuth actually found is of the order of magnitude of that to be expected on the assumption that actinium bismuth is stable. Should actinium bismuth be unstable, then clearly the Bi/U ratio should be about the same for all fresh unaltered minerals of whatever age. If, on the other hand, it is a stable product, the Bi/U ratio should be constant for minerals of the same age, but it should vary directly with the geological age of the mineral. It is worthy of notice that if actinium bismuth is a stable product, so that appreciable quantities of it can be extracted from uranium minerals, it should be found to have an atomic weight of 210 or 206, both of which values differ by two units from the atomic weight of ordinary bismuth. This method would appear to be a hopeful one for the question in hand, since a result lying near 210 or 206 would not only point to bismuth as the end product of actinium, but it would also give a means of deciding between 230 and 226 as the atomic weight of actinium. The occurrence of bismuth in radioactive minerals has already been commented upon, and it is to be hoped that in the near future more definite evidence for or against bismuth as the end product of actinium will be forthcoming.

The occurrence of thallium in radioactive minerals has also been noted. For instance, Exner and Haschek * found it to be present spectroscopically in appreciable quantities in pitchblende from Cornwall. The fact that if actinium bismuth is unstable, disintegrating with loss of an α ray, we should have a thallium isotope, renders thallium a possible end product of actinium. The analysis of a series of uranium minerals for uranium and thallium would be necessary to test this suggestion. The method of showing whether this thallium product is stable or unstable is the same as that suggested in the case of bismuth last treated. Further, in this case, the atomic weight of the thallium should be 206 or 202, instead of the atomic weight 204 of ordinary thallium. It is doubtful whether we are justified in laying very much

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* Exner and Haschek, *Wien. Sitzungsber.* cxxi. p. 1077 (1912).

stress on the occurrence of thallium in the Cornwall pitch-
blende, since this is of a very impure nature. Professor
Hönigschmid informs us that he has been unable to find
appreciable traces of thallium in selected pitchblende from
Joachimstal. Now the atomic weights of the lead from
pitchblende from these two districts are respectively 206·86
and 206·40, results which indicate the greater purity of the
Joachimstal material. It would thus appear that the sug-
gestion regarding thallium as the end product of actinium is
highly improbable.

§ 14. Conclusions.

(*a*) In Part I. of this paper it was shown from the uranium,
thorium, and lead contents of four series of radioactive
minerals:

(1) That the lead-uranium ratio is remarkably constant in
minerals of the same age, and varies sympathetically
with the geological age of minerals of different
antiquities, so that radium G may be regarded as
stable or practically so. It appears impossible that
any slight instability that may exist could ever be
definitely detected. The slight deviations in the
values of the Pb/U ratios are such as can be readily
accounted for by the presence of traces of original
lead, by the presence of the unstable thorium-lead,
and by the possible alterations which the minerals
may have suffered since their original crystallization.

(2) That thorium-lead does not tend to accumulate in
geological time, *i. e.* thorium E is an unstable
product.

(3) That the Pb/U ratios may be used as before and with
greater certainty for the determination of geological
time and the gradual construction of a complete
geological time-scale.

(*b*) On the assumption that the total lead present in the
minerals is made up of three constituents: (*a*) Uranium
lead (radium G); (*b*) Thorium lead (thorium E); and (*c*)
Original lead, it has been shown how the results obtained
can be applied to find the half-period of thorium E. This
has been found tentatively to be about 10^6 years.

(*c*) It has been suggested that the disintegration of
thorium E may be accompanied by the loss of a β ray, so
that the resulting product would be an isotope of bismuth.
Evidence has, however, been brought forward which suggests
that the latter cannot be a stable end product. Should this

Group V. *b* product of thorium be unstable, the method here used for thorium E could be applied to find its disintegration constant, when the bismuth and thorium contents of suitable minerals are known. Information could thus be obtained as to the next succeeding product, which would be a thallium isotope if the bismuth isotope disintegrates with loss of an α ray, or a polonium isotope if the change takes place with loss of a β ray.

(*d*) The evidence of atomic weight determinations of lead extracted from radioactive minerals also points to the stability of radium G, and the instability of thorium E. It has been shown that the most suitable mineral for the determination of the atomic weight of radium G is a geologically old, primary, fresh, uranium mineral. Using such a mineral, bröggerite, Hönigschmid and St. Horovitz found the value 206·06. Should actinium lead have an atomic weight of 210, the above result for bröggerite would indicate that it is unstable. Experiments to throw light on the stability of actinium lead are suggested in § 13. If the atomic weight of actinium lead is 206, we are unable to say whether it is unstable or not. Methods of attacking the question of the end product of actinium have been suggested, and it has been shown how one of these might incidentally throw light on the atomic weight of actinium. For thorium E it would appear that no very definite conclusions can be drawn from atomic weight determinations, owing to the instability of this element. In the most favourable circumstances, a value of about 207 would be obtained, instead of the theoretical value 208·4. Determinations of the atomic weights of bismuth and thallium from uranium and thorium minerals, would serve a useful purpose in supplying definite information regarding the end products of thorium and actinium.

(*e*) Atomic weight estimations can now be used to correct the crude determination of the age of a mineral by means of its present lead and uranium contents. Corrections must be applied both for original lead, which may be considerable (*e. g.* in some specimens of thorianite from Ceylon), and for a small equilibrium amount of thorium lead. These corrections appear to make very little difference to the time-scale as at present constituted. That this is true for the Devonian minerals of Norway we have already seen. The pre-Jatulian minerals of the Moss district of Norway require practically no correction, for bröggerite from that district contains uranium lead in an almost uncontaminated state, as shown by the atomic weight of lead prepared from the

mineral (206·06 found ; 206·2 theoretical value). As more evidence accumulates, the ratios for other geological periods will be similarly tested. At present it would seem that the age of the older intrusive rocks of Ceylon, as deduced from Pb/U ratios in thorianite and thorite, is probably too high. These ratios are nearly always greater than 0·2, giving an age exceeding 1600 million years. Zircon from the same pegmatites, however, gives a ratio of 0·164 (1370 million years), which seems to be more probable, in the light of atomic weight estimations. Zircon is much less likely to contain original lead than thorite or thorianite, and apart from the difficulty of estimating the very small quantities of lead which have accumulated, zircon represents one of the most valuable minerals for age determinations.

Finally, in addition to our previous acknowledgments to Professors Strutt and Mache, we wish to express our thanks to Professor Stefan Meyer, for his kindly interest and encouragement during the progress of this work.

LXXII. *On Ripples.* By J. R. Wilton, *M.A., D.Sc., Assistant Lecturer in Mathematics at the University of Sheffield* [*].

IN carrying the approximation to the form of a wave to such an extent as is done in my paper on "On Deep Water Waves" (Phil. Mag. Feb. 1914, pp. 385–394), which will here be referred to as " Waves," it is important to make certain that the sense of accuracy thus obtained is not illusory. The present paper therefore takes up the consideration of the corrections which have to be applied. We shall, however, still suppose that the wave (or ripple) is formed under ideal conditions,—that there is no wind, no secondary disturbance of any kind,—that the "ocean" is "deep" (a depth of ten centimetres will be ample for the ripples we shall actually consider) and of unlimited extent. With this understanding there are three things for which we have to make allowance, namely :—

(1) Surface Tension,
(2) The formation of waves in the air,
(3) Viscosity.

Now the first order approximation to the velocity when (1) and (2) are taken into account is known to be given by

$$c^2 = \frac{g\lambda}{2\pi} \frac{\rho - \rho'}{\rho + \rho'} + \frac{2\pi}{\lambda} \frac{T}{\rho + \rho'},$$

in which ρ is the density of water, ρ' of the air, T is the surface tension, and the rest of the notation is that of " Waves."

It is assumed in obtaining the above value of c^2 that the air is incompressible, but the removal of this restriction will rather lessen than increase the effect of air waves.

Since ρ'/ρ is small the effect of ρ' is to multiply one term in c^2 by $12 - \rho'/\rho$, the other by $1 - \rho'/\rho$. Now

$$\rho'/\rho = \cdot0013$$

nearly. Hence the correction is of the order 1/400 of the uncorrected value. We shall consider this as negligible. In fact, in such a (relatively) high wave as that of " Waves," fig. 1, the ratio of the last term retained to the first is of the order

$$A_{12}/A_1 = 1/150.$$

If, then, we omit ρ', we have as a first approximation

$$\frac{2\pi c^2}{g\lambda} = 1 + \left(\frac{2\pi}{\lambda}\right)^2 \frac{T}{g\rho},$$

which we shall, for brevity, write in the form

$$\mu = 1 + \kappa.$$

But

$$T/g\rho = 74/981 = \cdot075,$$

so that κ, the correction due to surface tension, is appreciable for waves of length less than about 25 cm., and for very short ripples it may become very large.

Finally, we have to take account of viscosity. It is shown in Lamb's 'Hydrodynamics,' § 332, p. 566 (Third Edition). that, if $\lambda/\cdot0048$ cm. may be considered large (say 10 or more), the effect of viscosity is to introduce a time factor $e^{-2\nu(2\pi/\lambda)^2 t}$ which does not affect the *form* of the wave, and to introduce a correcting factor to the form of the wave of the order of magnitude

$$\tau = \frac{2\nu(2\pi/\lambda)^2}{\sqrt{\dfrac{g\lambda}{2\pi} + \dfrac{2\pi}{\lambda}\dfrac{T}{\rho}}} = \frac{2\nu g^{-\frac{1}{2}}(2\pi/\lambda)^{\frac{5}{2}}}{\sqrt{1+\kappa}},$$

ν being the coefficient of dynamical viscosity.

The following table will show that surface tension is always of considerably greater effect than viscosity *.

Wave length, λ.	Suface Tension Correction, κ.	Viscosity Correction, τ.	Ratio, κ/τ.
9·4 cm.	·033	·0004	80
6·3 ,, ...	·075	·0011	68
3·1 ,, ...	·30	·006	50
1·6 ,, ...	1·2	·03	40
·8 ,, ...	4·8	·11	44
·4 ,, ...	19	·36	53

Thus κ/τ is never less than 40, so that we may neglect viscosity even for small ripples without risk of serious error, provided always that the condition that $\lambda/\cdot0048$ is to be " large " is not forgotten†. But for longer waves the correction due to the formation of air waves is of the same order of magnitude as κ : thus, when $\lambda = 35$ cm.,

$$\kappa = 1/400,$$

nearly. Hence, if we include T but omit the other two corrections, we must apply our results only to ripples and waves of from, say, 1 mm. to 20 cm. in length, so that the form of waves which ordinarily occur in the open sea will not be affected by any of these considerations. We shall, actually, apply our formulæ only to ripples of from 5 mm. to 25 mm. in length. With this understanding we proceed to determine the form of a wave when surface tension is taken into account.

Let R be the radius of curvature of the wave : R will be reckoned positive when the concavity is upwards. Then, if Π is the atmospheric pressure, the pressure along the free surface, within the water, is

$$p = \Pi - T/R,$$

* It will be observed that for ripples, down to half a centimetre in length, we may still speak of the correction due to viscosity, but it is absurd to speak of the " correction " due to surface tension, for the latter is the predominating influence in determining the form of ripples of 2 cm. length, or less.

† The viscous *time* factor is, however, far from being negligible for short ripples.

and the surface condition becomes *

$$\dot{\phi} + \tfrac{1}{2}q^2 = gy + \mathrm{T}/\rho\,\mathrm{R} - \tfrac{1}{2}\mathrm{C}'. \quad . \quad . \quad . \quad . \quad (1)$$

To determine the form of the term $\mathrm{T}/\rho\mathrm{R}$ we expand $1/\mathrm{R}$ in a series of cosines of multiples of ξ by means of the equations for x and y on p. 392 of "Waves." Since on the free surface $\xi' = \xi$, we have

$$\frac{1}{\mathrm{R}} = \frac{2\pi\iota}{\lambda}\left(\frac{d\eta}{d\xi}\frac{d^2\eta'}{d\xi^2} - \frac{d\eta'}{d\xi}\frac{d^2\eta}{d\xi^2}\right)\Big/\left(\frac{d\eta}{d\xi}\frac{d\eta'}{d\xi}\right)^{3/2}.$$

The sign is determined by the fact that R is positive at the trough of the wave where $\xi = 0$. $\mathrm{A}_1, = -a$, is negative, and therefore the predominant term in $1/\mathrm{R}$ is $2\pi a/\lambda$, which is positive.

On substituting in (1) we find, as in "Waves," p. 387,

$$0 = \tfrac{1}{2}\mu + \left\{ \mathrm{C} + \sum_1^\infty \mathrm{A}_n \cos n\xi \right\}\left\{(1 + \sum_1^\infty n\mathrm{A}_n \cos n\xi)^2 + (\sum_1^\infty n\mathrm{A}_n \sin n\xi)^2\right\}$$

$$+ \kappa\left\{\sum_1^\infty n^2\mathrm{A}_n \cos n\xi + \sum_1^\infty n^3\mathrm{A}_n^2\right.$$

$$\left. + \sum_{m=1}^\infty \sum_{n=m+1}^\infty mn(m+n)\mathrm{A}_m\mathrm{A}_n \cos(m-n)\xi\right\}$$

$$\left\{(1 + \sum_1^\infty n\mathrm{A}_n \cos n\xi)^2 + (\sum_1^\infty n\mathrm{A}_n \sin n\xi)^2\right\}^{-\frac{1}{2}}, \quad . \quad (2)$$

where, as before,

$$\mu = \frac{2\pi c^2}{g\lambda}, \quad \kappa = \left(\frac{2\pi}{\lambda}\right)^2\frac{\mathrm{T}}{g\rho}.$$

As a first approximation we see that

$$\mathrm{C} + \tfrac{1}{2}\mu = 0,$$

$$\mathrm{A}_1(1 + 2\mathrm{C} + \kappa) = 0,$$

so that A_1 is arbitrary,

$$\mathrm{A}_1 = -a, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and

$$c^2 = \frac{g\lambda}{2\pi}(1 + \kappa),$$

as it should.

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* The explanation of any notation not given in this paper will be found in "Waves," pp. 385–6.

To obtain closer approximations we must expand the right hand side of (2) and re-arrange in cosines of multiples of ξ, The coefficient of $\cos n\xi$ is then to be equated to zero. It would be possible to obtain the general form of the equation thus derived, but it would be extremely complicated and there would be no advantage in doing this. We shall therefore write down the resulting equations only in so far as they are necessary to obtain the approximation we desire. We shall determine each approximation accurately so far as T is concerned.

The equations derived from (2) are, if we retain terms of the fifth order and reject those of higher orders,

$$\mu + 2C(1 + A_1^2 + 4A_2^2) + 2A_1^2 + 4A_2^2 + 4A_1^2 A_2$$

$$+ \kappa(A_1^2 + \frac{1}{8}A_1^4 - 2A_1^2 A_2 + 8A_2^2) = 0, \quad . \quad . \quad (4)$$

$$2C(A_1 + 2A_1 A_2 + 6A_2 A_3) + A_1 + A_1^3 + 3A_1 A_2 + 5A_2 A_3 + 6A_1 A_2^2 + 3A_1^2 A_3$$

$$+ \kappa(A_1 - \frac{3}{8}A_1^3 + 3A_1 A_2 - \frac{5}{64}A_1^5 + \frac{5}{4}A_1^3 A_2 - \frac{15}{8}A_1^2 A_3 - 5A_1 A_2^2 + 15A_2 A_3)$$

$$= 0, \quad . \quad (5)$$

$$2C(2A_2 + 3A_1 A_3) + A_2 + A_1^2 + 3A_1^2 A_2 + 4A_1 A_3$$

$$+ \kappa(4A_2 - \frac{1}{2}A_1^2 + \frac{1}{4}A_1^4 - 2A_1^2 A_2 + 6A_1 A_3) = 0, \quad . \quad . \quad (6)$$

$$2C(3A_3 + 4A_1 A_4) + A_3 + 3A_1 A_2 + 5A_1 A_4 + 4A_1^2 A_3 + 2A_1 A_2^2$$

$$+ \kappa(9A_3 + \frac{3}{8}A_1^3 - 3A_1 A_2 - \frac{25}{128}A_1^5 + \frac{15}{8}A_1^3 A_2 - \frac{15}{4}A_1^2 A_3$$

$$- \frac{5}{2}A_1 A_2^2 + 10A_1 A_4) = 0, \quad . \quad (7)$$

$$8CA_4 + A_4 + 4A_1 A_3 + 2A_2^2$$

$$+ \kappa(16A_4 - \frac{5}{16}A_1^4 - 4A_2^2 + 3A_1^2 A_2 - 6A_1 A_3) = 0, \quad . \quad (8)$$

$$10CA_5 + A_5 + 5A_1 A_4 + 5A_2 A_3$$

$$+ \kappa(25A_5 + \frac{35}{128}A_1^5 - \frac{25}{8}A_1^3 A_2 + \frac{45}{8}A_1^2 A_3 + \frac{15}{2}A_1 A_2^2 - 10A_1 A_4 - 15A_2 A_3)$$

$$= 0. \quad . \quad (9)$$

From these equations, remembering (3), I find by successive approximation :—

$$A_1 = -a,$$

$$A_2 = \frac{1}{2}\frac{\kappa-2}{2\kappa-1}a^2 - \frac{1}{16}\frac{30\kappa^3-71\kappa^2+17\kappa-8}{(2\kappa-1)^3(3\kappa-1)}a^4, \quad \cdot \quad \cdot \quad \cdot \quad (10)$$

$$A_3 = -\frac{3}{16}\frac{2\kappa^2-11\kappa+8}{(2\kappa-1)(3\kappa-1)}a^3$$
$$+ \frac{13248\kappa^5-53640\kappa^4+63260\kappa^3-29010\kappa^2+7971\kappa-1216}{768(2\kappa-1)^3(3\kappa-1)^2(4\kappa-1)}a^5, \quad . \quad (11)$$

$$A_4 = \frac{18\kappa^3-183\kappa^2+361\kappa-128}{48(2\kappa-1)(3\kappa-1)(4\kappa-1)}a^4, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (12)$$

$$A_5 = -\frac{5}{1536}\frac{288\kappa^5-4680\kappa^4+18980\kappa^3-24786\kappa^2+11091\kappa-1600}{(2\kappa-1)^2(3\kappa-1)(4\kappa-1)(5\kappa-1)}a^5, \quad . \quad (13)$$

$$C = -\frac{1}{2}-\frac{1}{2}\kappa+\frac{1}{16}\frac{2\kappa^2-15\kappa+16}{2\kappa-1}a^2$$
$$-\frac{1}{256}\frac{24\kappa^5+220\kappa^4-2422\kappa^3+4701\kappa^2-2858\kappa+704}{(2\kappa-1)^3(3\kappa-1)}a^4, \quad \cdot \quad \cdot \quad (14)$$

$$\mu = 1+\kappa-\frac{1}{8}\frac{2\kappa^2+\kappa+8}{2\kappa-1}a^2$$
$$+\frac{1}{128}\frac{24\kappa^5-164\kappa^4-566\kappa^3+1821\kappa^2-1322\kappa+448}{(2\kappa-1)^3(3\kappa-1)}a^4. \quad \cdot \quad \cdot \quad \cdot \quad (15)$$

I have also calculated, independently, the values of these constants in the particular cases $\kappa=1$ and $\kappa=2$.

When $\kappa=1$, $A_1=-a$,

$$A_2 = -\frac{1}{2}a^2+a^4, \quad A_3 = \frac{3}{32}a^3+\frac{613}{9216}a^5,$$

$$A_4 = \frac{17}{72}a^4, \quad A_5 = \frac{3535}{36864}a^5, \quad \left.\right\} \quad . \quad (16)$$

$$C = -1+\frac{3}{16}a^2-\frac{369}{512}a^4, \quad \mu = 2-\frac{11}{8}a^2+\frac{241}{256}a^4.$$

When $\kappa=2$, $A_1=-a$,

$$A_2 = \frac{1}{120}a^4, \quad A_3 = \frac{3}{40}a^3-\frac{547}{67200}a^5,$$

$$A_4 = \frac{1}{840}a^4, \quad A_5 = -\frac{47}{5376}a^5, \quad \left.\right\} \quad . \quad (17)$$

$$C = -\frac{3}{2}-\frac{1}{8}a^2+\frac{3}{80}a^4, \quad \mu = 3-\frac{3}{4}a^2-\frac{3}{40}a^4.$$

It will be found that equations $(10), \ldots (15)$ agree with
(16) and (17), and that they also agree with the known
result when $\kappa = 0$.   Hence it is improbable that there is any
undetected error in calculation.

The most interesting thing about the constants whose
values are given in equations $(10), \ldots (15)$ is the unexpected
form of the denominators.   It is easy to see that this form
is general; for the coefficient of A_n in the equation which
determines it is

$$2n\mathrm{C} + 1 + n^2\kappa = n^2\kappa + 1 - n(1+\kappa)$$
$$= (n-1)(n\kappa - 1),$$

to a first approximation.   Hence the denominator of A_n
contains as a factor $(n-1)! \prod_{r=1}^{n} (r\kappa - 1)$.   Now we have seen
that we are justified in neglecting the effect of air waves
if κ is greater than about $\cdot 01$; so that for a considerable
range of values of n we have to consider the possibility
of values of κ of the form $\kappa = 1/n$, where n is a positive
integer.   To the consideration of these values of κ we shall
return later.   On the other hand, since we are not justified
in neglecting the effect of air-waves if κ is less than about
$\cdot 01$, we cannot, as might appear at first sight from equations
$(10), \ldots (15)$, conclude that however small κ is, so long as it
is finite, the value of one of the coefficients A_n becomes
illusory, and therefore that the ordinary theory, in which
$\kappa = 0$, is incorrect.

Let us take first the case of a ripple whose form is largely
determined by surface tension—say that for which $\kappa = 10$,
and therefore $\lambda = \cdot 54$ cm.   From equations $(10), \ldots (15)$
I find, for this ripple,

$$A_1 = -a, \qquad A_2 = \cdot 21 a^2 - \cdot 0072 a^4,$$
$$A_3 = -\cdot 033 a^3 + \cdot 0049 a^5, \qquad A_4 = \cdot 0031 a^4, \qquad A_5 = \cdot 00023 a^5,$$
$$\mu = 11 - 1 \cdot 43 a^2 + \cdot 014 a^4.$$

The largest value of a which we may safely insert in these
equations is * $a = 1 \cdot 5$.   We then find

$$A_1 = -1 \cdot 5, \qquad A_2 = \cdot 44, \qquad A_3 = -\cdot 075,$$
$$A_4 = \cdot 016, \qquad A_5 = \cdot 0017,$$
$$\mu = 7 \cdot 85, \ \text{i. e.,} \ c = 25 \cdot 7 \ \text{cm./sec.,}$$
$$\lambda = \cdot 54 \ \text{cm.}$$

* It may be verified that R is positive for this value of a when $\xi = 0$.

The corresponding values of x and y are (" Waves," p. 392) given by

$$ct - x = {\cdot}086(\xi - 1{\cdot}5 \sin \xi + {\cdot}44 \sin 2\xi - {\cdot}075 \sin 3\xi$$
$$+ {\cdot}016 \sin 4\xi + {\cdot}0017 \sin 5\xi),$$

$$y = {\cdot}086(1{\cdot}5 \cos \xi - {\cdot}44 \cos 2\xi + {\cdot}075 \cos 3\xi$$
$$- {\cdot}016 \cos 4\xi - {\cdot}0017 \cos 5\xi).$$

Corresponding values of x and y are given in Table I., and the ripple is drawn in fig. 1.

TABLE I.

Ripple of wave-length ·54 cm.

ξ.	$ct - x$.	y.
0	0	·095
$\pi/6$	·008	·094
$\pi/3$	·009	·077
$\pi/2$	·013	·037
$2\pi/3$	·037	—·039
$5\pi/6$	·128	−·129
π	·272	−·175

Fig. 1.

Ripple of length ·54 cm.; amplitude ·27 cm.; velocity 25·7 cm./sec.

N.B.—The scale of this figure is just twice that of those given below : it is about 7·1 to 1.

Let us now take the rather longer ripples $\kappa = 2$ and $\kappa = 1$.

First, when $\kappa = 2$ the constants A_1, &c. are given by equations (17). In the particular case when $a = 1$, which

is a relatively high ripple, we have

$$\kappa = 2, \quad \lambda = 1 \cdot 22 \text{ cm.}, \quad \lambda/2\pi = \cdot 194,$$
$$A_1 = -1, \quad A_2 = \cdot 0083, \quad A_3 = \cdot 067, \quad A_4 = \cdot 0012,$$
$$A_5 = -\cdot 0087,$$
$$\mu = 2 \cdot 18, \quad c = 20 \cdot 3 \text{ cm./sec.}$$

Corresponding values of x and y are given in Table II., and the ripple is shown in fig. 2.

TABLE II.

Ripple of wave-length 1·22 cm.

ξ.	$ct - x$.	y.
0	0	·181
$\pi/6$	·018	·165
$\pi/3$	·038	·111
$\pi/2$	·096	·001
$2\pi/3$	·239	−·110
$5\pi/6$	·421	−·167
π	·611	−·185

Fig. 2.

Ripple of length 1·22 cm.; amplitude ·37 cm.; velocity 20·3 cm./sec.

Again, when $\kappa = 1$ we find A_1, &c. from equations (16). Taking in this case $a = 1/3$, we find

$$\kappa = 1, \quad \lambda = 1 \cdot 31 \text{ cm.}, \quad \lambda/2\pi = \cdot 208,$$
$$A_1 = -\cdot 333, \quad A_2 = -\cdot 043, \quad A_3 = \cdot 0037, \quad A_4 = \cdot 0029,$$
$$A_5 = \cdot 0004,$$
$$\mu = 1 \cdot 85, \quad c = 19 \cdot 4 \text{ cm./sec.}$$

Corresponding values of x and y are given in Table III. and the ripple is drawn in fig. 3.

TABLE III.

Ripple of wave-length 1·31 cm.

ξ.	$ct-x$.	y.
0	0	·077
$\pi/6$	·068	·068
$\pi/3$	·144	·031
$\pi/2$	·258	−·009
$2\pi/3$	·389	−·039
$5\pi/6$	·522	−·054
π	·653	−·060

Fig. 3.

Ripple of length 1·31 cm. ; amplitude ·14 cm.; velocity 19·4 cm./sec.

We come now to the most interesting portion of our inquiry,—the consideration of the form of those waves for which κ is the reciprocal of a positive integer n other than unity. When κ is not actually equal to $1/n$, it is always possible to choose a sufficiently small to insure the convergence of the series for A_2, A_3, ... For it is easy to satisfy oneself that the index of the power of $n\kappa - 1$ in the denominator of any coefficient is less than the index of the power of a which it multiplies. Hence if we put $a = (n\kappa - 1)b$, some power of $n\kappa - 1$ will divide every coefficient A_m, and it is now manifestly possible to choose a value of b which secures convergence of the series. If $n\kappa - 1$ is small a will be small, *i. e.* the amplitude of the wave will be small ; but as A_n and the succeeding coefficients become relatively important the form of the wave may be very different from that of a simple cosine curve.

When $\kappa = 1/n$ the case is different. The ordinary method of approximation breaks down altogether, and we have to start again *ab initio*. We shall consider in particular the case $\kappa = \frac{1}{2}$.

When $\kappa = \frac{1}{2}$, to a first approximation $C = -\frac{3}{4}$, and therefore equation (6) leads to

$$\tfrac{3}{4}A_1{}^2 + \text{terms of order higher than the second} = 0.$$

Hence A_1 cannot be of the first order unless A_2 is of the

same order. But if A_2 is of the first order, the second approximation to (5) is

$$(2C + \tfrac{3}{2})A_1 + \tfrac{3}{2}A_1 A_2 = 0,$$

i. e., $$C = -\tfrac{3}{4} - \tfrac{3}{4}A_2;$$

and substituting in (6) we have, to the second order,

$$-3A_2{}^2 + \tfrac{3}{4}A_1{}^2 = 0,$$

i. e., $$A_2 = \pm \tfrac{1}{2}A_1.$$

From equations (7), (8), and (9) we see that, if A_1 and A_2 are both of the first order, A_3 and A_4 are both of the second order, A_5 and A_6 are both of the third order, and so on.

If $\kappa = 1/3$, it is easy to see that we may take the orders of the successive coefficients to be

$$1, 2 ; \quad 1, 2, 3 ; \quad 2, 3, 4 ; \quad 3, 4, 5 ; \ldots .$$

While in the general case, when $\kappa = 1/n$, the orders are

$$1, 2, 3, \ldots n-1 ; \quad n-2, n-1, n \ldots 2n-3 ;$$
$$2n-4, 2n-2, \ldots 3n-5 ; \quad 3n-6, \ldots$$

It is only in the particular case of $\tfrac{1}{2}\kappa =$, *i. e.* $n = 2$, that there is any ambiguity in the form of A_n.

Let us return now to the consideration of the case $\kappa = \tfrac{1}{2}$. To the first order we have

$$A_1 = -a, \quad A_2 = \pm \tfrac{1}{2}a.$$

And, on substituting these values in the other equations, we find as a first approximation,

$$A_1 = -a, \quad A_2 = \pm \tfrac{1}{2}a, \quad A_3 = \pm \tfrac{3}{4}a^2, \quad A_4 = 0, \quad A_5 = 0,$$
$$C = -\tfrac{3}{4} \mp \tfrac{3}{8}a, \quad \mu = \tfrac{3}{2} \pm \tfrac{3}{4}a.$$

As a second approximation I find, after rather long analysis,

$$A_1 = -a, \quad A_2 = \pm \tfrac{1}{2}a - \tfrac{1}{8}a^2, \quad A_3 = \pm \tfrac{3}{4}a^2 + \tfrac{15}{8}a^3,$$
$$A_4 = \mp \tfrac{1}{2}a^2, \quad A_5 = 0, \quad A_6 = \mp \tfrac{3}{80}a^3,$$
$$C = -\tfrac{3}{4} \mp \tfrac{3}{8}a + \tfrac{9}{32}a^2, \quad \mu = \tfrac{3}{2} \pm \tfrac{3}{4}a - \tfrac{25}{16}a^2.$$

In particular, when $a = \cdot 2$ the two sets of values are :—

(1) $A_1 = -\cdot 2, \quad A_2 = \cdot 095, \quad A_3 = \cdot 045, \quad A_4 = -\cdot 004,$
$$A_5 = 0, \qquad A_6 = -\cdot 0003,$$
$$\mu = 1 \cdot 59, \quad c = 24 \cdot 6 \text{ cm./sec.}$$

(2) $A_1 = -\cdot 2, \quad A_2 = -\cdot 105, \quad A_3 = -\cdot 015, \quad A_4 = \cdot 004,$
$$A_5 = 0, \quad A_6 = \cdot 0003,$$
$$\mu = 1 \cdot 29, \quad c = 22 \cdot 2 \text{ cm./sec.}$$

The two corresponding sets of values of x and y are given in Tables IV. *a* and IV. *b*, and the ripples* are shown in figs. 4 *a* and 4 *b*, respectively.

TABLE IV.

Ripple of length 2·44 cm.

	a.				*b*.		
ξ.	$ct - x$.	y.		ξ.	$ct - x$.	y.
0	0	·025		0	0	·123
$\pi/6$	·21	·050		$\pi/6$	·12	·088
$\pi/3$	·37	·087		$\pi/3$	·30	·014
$\pi/2$	·52	·038		$\pi/2$	·54	− ·042
$2\pi/3$	·71	− ·039		$2\pi/3$	·78	− ·052
$5\pi/6$	·96	− ·086		$5\pi/6$	1·00	− ·046
π	1·22	− ·095		π	1·22	− ·044

Fig. 4 *a*.

Ripple of length 2·44 cm.; amplitude ·182 cm.; velocity 24·6 cm./sec.

Fig. 4 *b*.
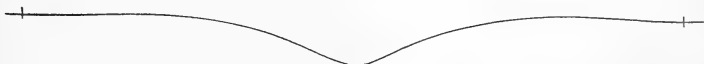
Ripple of length 2·44 cm.; amplitude ·175 cm.; velocity 22·2 cm./sec.

It is possible that the dimple at the crest of the second ripple is due only to the neglect of terms of higher order; but it seems very unlikely that the form of the first ripple can be due to this cause. One is tempted to say that 4 *a* is probably unstable, 4 *b* probably stable. In any case there is room for experimental investigation of the forms of ripples of this particular length, and also of the form of "high" ripples of very short wave-length, such as that shown in fig. 1. It would also be interesting to obtain experimentally the forms of the ripples whose lengths are given by $\kappa = 1 3$, $\kappa = 1/4$, &c.

* I have not strictly adhered to the customary distinction between ripples and waves.

It must, however, be remembered that although viscosity does not, to any appreciable extent, affect the forms of these ripples, it does very rapidly damp them out. Thus the amplitude of the ripple in fig. 1 is halved in less than one fifth of a second, so that it must be sought within a very few centimetres of the generating source. But, if the ripples of fig. 4 could be produced, they might be expected to travel some twenty or thirty centimetres without any serious diminution of amplitude.

LXXIII. *On the Operator* ∇ *in Combination with Homogeneous Functions.* By Frank L. Hitchcock, *Ph.D.*[*]

1. AMONG the uses of the Hamiltonian operator ∇ there are three which are particularly remarkable. First is the use of ∇ to distinguish the character of fields of force, fluid motion, and other vector fields. Second is its use to express integral relations having to do with space-integration over surfaces and volumes. Third, when ∇ is combined with functions which are homogeneous in the point-vector ρ, many new results are obtained.

To recall the leading facts under the first category:—If a vector function F of the point-vector ρ satisfies the relation $V\nabla F = 0$, its rotation vector or "curl" is zero, and its distribution is lamellar. If $S\nabla F = 0$, the "divergence" is zero, and the distribution solenoidal. If both these relations hold, so that $\nabla F = 0$, the distribution is Laplacean. If F is everywhere at right angles to its own curl, we have $SF\nabla F = 0$; as I am not aware of any name for such a distribution, I shall venture to call it ORTHOGYRAL [†]. The most significant property of an orthogyral vector is that it becomes lamellar when multiplied by a suitably chosen variable scalar [‡].

Under the second category fall the quaternionic forms of the theorems of Gauss and of Stokes on multiple integrals, which have been greatly extended by the late Profs. Tait and C. J. Joly and by Dr. Alex. McAulay.

My present object is to develop somewhat further the uses

of ∇ in the third of the above ways,—in combination with homogeneous functional operations. A few facts are already known: chief of which is Euler's theorem, written in quaternion form as

$$S\rho\nabla \,.\, F\rho = -nF\rho, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $F\rho$ is any function of ρ (scalar or vector), homogeneous of degree n in ρ. Aside from Euler's theorem, most of the known results on homogeneous functions in connexion with ∇ are combinations of ∇ with linear vector operators, and are due to the writers above mentioned. For example, if $dF\rho = \phi d\rho$, and if ϕ' is the linear vector operator conjugate to ϕ, then

$$\phi'\alpha - \phi\alpha = V\alpha V\nabla F\rho, \quad . \quad . \quad . \quad . \quad (2)$$

where α is any vector not acted on by ∇^*.

2. Before proceeding to the proof of new theorems, it will be necessary to enter briefly into a few elementary considerations. First, with regard to notation, I shall write, for brevity, $T\rho = r$ and $U\rho = u$, so that $\rho = ru$.

Next, as to the definition of a homogeneous function, it is most natural for a vector algebraist to write

$$F\rho = r^n Fu, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

as the definition of homogeneity, either for scalar or vector. This is of course precisely equivalent to the usual definition, and much more available. In words: A homogeneous function of ρ is one that can be factored into a power of r (that is $T\rho$), and a function of u (that is $U\rho$), alone.

The differentials of $T\rho$ and of $U\rho$ are important, and may be expanded in many forms (Tait, Art. 140). For the present purpose we may take as most convenient for the tensor of ρ,

$$dr = -Sud\rho, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and for the unit vector

$$du = r^{-1}(d\rho + uSud\rho). \quad . \quad . \quad . \quad . \quad (5)$$

Again, we often need to apply ∇ to a function of u alone. This is achieved by writing

$$dF\rho = \phi d\rho. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

We then have

$$dFu = \phi du$$
$$= \phi(d\rho + uSud\rho)r^{-1}, \text{ by (5).}$$

* Tait, 'Quaternions,' 3rd Ed., Arts. 185, 186.

We now obtain ∇Fu from dFu by changing $d\rho$ into ρ', at the same time writing ∇' to the left of the whole. That is

$$\nabla Fu = \nabla'\phi(\rho' + uS u\rho')r^{-1}, \quad . \quad . \quad . \quad (7)$$

where the accents indicate that ∇ acts only on the accented ρ. The expression ∇Fu therefore stands always for a function homogeneous of degree -1. This holds when $F\rho$ is either scalar or vector, since the foregoing identities depend only on the linear character of ϕ and not upon its dimensionality.

Finally, if $F\rho$ is homogeneous of degree n in ρ, $\nabla F\rho$ is homogeneous of degree $n-1$. For

$$\nabla F\rho = \nabla (r^n Fu), \text{ by definition,}$$
$$= nr^{n-1}\nabla r \,.\, Fu + r^n \nabla Fu, \text{ by distributing } \nabla;$$

but, in the first term on the right, $\nabla r = u$ (by Tait, Art. 145), and in the second term, ∇Fu, as has been shown, is homogeneous of degree -1. Hence the right side may be factored into r^{n-1} and a function of u alone. It is therefore, by definition, homogeneous of degree $n-1$. This, also, holds for scalar or for vector.

3. I shall now prove the following theorem in regard to solenoidal vectors:—

Any homogeneous vector may be rendered solenoidal by adding to it a term of the form ρt, where t is a properly chosen scalar; exception must be made of vectors of degree -2.

For consider the effect of ∇ upon the vector $\rho S \nabla F\rho$, where $F\rho$ is a vector homogeneous of degree n in ρ. We have

$$\nabla(\rho S\nabla F\rho) = \nabla\rho \,.\, S\nabla F\rho + \nabla S\nabla F\rho \,.\, \rho, \text{ by distributing } \nabla.$$

But, in the first term on the right, $\nabla\rho = -3$. Furthermore, scalars are commutative, so that if we take the scalar part of both sides we may write

$$S\nabla(\rho S\nabla F\rho) = -3S\nabla F\rho + S\rho\nabla \,.\, S\nabla F\rho.$$

Now the scalar $S\nabla F\rho$, as already pointed out, is of degree $n-1$. We may therefore apply Euler's theorem to the right-hand term, and have, (by (1)),

$$S\rho\nabla \,.\, S\nabla F\rho = -(n-1)S\nabla F\rho.$$

By combining terms, therefore,

$$S\nabla(\rho S\nabla F\rho) = -(n+2)S\nabla F\rho. \quad . \quad . \quad (8)$$

The following identity will now be evident,

$$S\nabla \left\{ F\rho + \frac{\rho S\nabla F\rho}{n+2} \right\} = 0, \quad \ldots \quad (9)$$

$F\rho$ being a vector homogeneous in ρ of degree other than -2. This identity proves the theorem and shows how to find the scalar t.

The term ρt is uniquely determined. For if there were two values, their difference would be a scalar multiple of ρ and would be solenoidal. Call this difference ρt_1. But by the same order of reasoning as above, $S\nabla(\rho t_1) = -(n+2)t_1$, which cannot vanish unless $t_1 = 0$ or $n = -2$*.

4. As a simple, but important, extension of the foregoing theorem, let us suppose (what is frequently the case) that a non-homogeneous vector can be written as the sum of several vector terms, each homogeneous in its own degree, *e. g.* let

$$F\rho = F_1\rho + F_2\rho + \ldots + F_n\rho + \ldots,$$

where the subscripts denote the degrees of their terms. By applying the theorem to the separate terms, we see that $F\rho$ may be rendered solenoidal by adding the vector

$$\rho S\nabla \left\{ \frac{F_1\rho}{3} + \frac{F_2\rho}{4} + \ldots + \frac{F_n\rho}{n+2} + \ldots \right\}.$$

The series concerned may be infinite, provided they are convergent.

Conversely (as an example of integration with ∇), if the convergence of a vector, $(S\nabla F\rho)$, be given, we can write down a value for the vector itself, which shall be a scalar multiple of ρ, provided we can expand the convergence as a sum of homogeneous scalar functions of ρ lacking a term of degree -3. For example, if we have given

$$\text{convergence} = S\nabla F\rho = t_0 + t_1 + t_2 + \ldots +,$$

where the subscripts denote the degrees of their terms, then a possible value of $F\rho$ having this convergence is

$$F\rho = -\rho \left\{ \frac{t_0}{3} + \frac{t_1}{4} + \frac{t_2}{5} + \ldots \right\},$$

a flux directed toward the origin.

5. These very simple results on the solenoidal character of vector fields may naturally lead us to inquire whether there

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* In a similar manner we may show that a term of the form ρt, if t is a scalar of degree -3 in ρ, is always solenoidal.

are not analogous facts in regard to lamellar vectors. The following is the case :—

Any homogeneous vector may be rendered lamellar by adding to it a term of the form $V\rho\tau$, where τ is a properly chosen vector ; exception must be made of vectors of degree -1.

For consider the well-known vector identity (Tait, Art. 90),

$$V\alpha V\beta\gamma = \gamma S\alpha\beta - \beta S\alpha\gamma.$$

Writing ρ for α, ∇ for β, and $F\rho$ for γ, this identity becomes

$$V\rho V\nabla F\rho = F\rho' \cdot S\rho\nabla' - \nabla'S\rho F\rho', \quad . \quad . \quad (10)$$

where, on the right, accents indicate that ∇ acts only on $F\rho$. By Euler's theorem, $F\rho' \cdot S\rho\nabla' = -nF\rho$. Also,

$$\nabla S\rho F\rho = \nabla S\rho'F\rho + \nabla'S\rho F\rho', \quad . \quad . \quad . \quad (11)$$

by distributing ∇. (Unaccented ∇ acts on all that follows in the same term.) But the first term on the right of (11) is the same as $-F\rho$, by Tait, Art. 146. Whence (11) becomes

$$\nabla S\rho F\rho = -F\rho + \nabla'S\rho F\rho'. \quad . \quad . \quad . \quad (12)$$

By adding (10) and (12) and solving for $F\rho$ we therefore have the identity

$$F\rho = -\frac{V\rho V\nabla F\rho}{n+1} - \frac{\nabla S\rho F\rho}{n+1}, \quad . \quad . \quad (13)$$

$F\rho$ being any vector homogeneous in ρ of degree other than -1. The right-hand term is obviously lamellar. Stated in words, (13) shows that any homogeneous vector field (exception noted) may be taken as the sum of two fields, one lamellar (irrotational), the other at right angles to the point vector. By transposing, and operating with $V\nabla$, (13) becomes

$$\cdots V\nabla \left\{ F\rho + \frac{V\rho V\nabla F\rho}{n+1} \right\} = 0. \quad . \quad . \quad (14)$$

This latter identity proves the proposition, and shows how to find the vector τ. The identity (14) may be verified by direct operation*.

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* The method used above for obtaining (14) is not quite parallel to that by which the analogous (9) was proved. Indeed, (9) might have been proved by first establishing the identity, analogous to (13),

$$(n+2)F\rho = -\rho S\nabla F\rho - V\nabla V\rho F\rho,$$

by expanding the last term on the right by the formula, Phil. Mag. June 1902, p. 579, (6). We then have (9) by the operator $S\nabla$; or we have (14) by writing $V\nabla F\rho$ in place of $F\rho$ which is any homogeneous vector, so making n become $n-1$.

The term $V\rho\tau$ is uniquely determined. For if there were two possible values their difference would be of the form $V\rho\tau_1$, and would be lamellar. Now the term $V\rho\tau_1$ is of degree n, hence τ_1 is of degree $n-1$. We therefore have identically[*]

$$V\nabla V\rho\tau_1 = -(n+1)\tau_1 - \rho S\nabla\tau_1 \quad . \quad . \quad . \quad (15)$$

If n does not equal -1, τ_1 does not have degree -2, and may be rendered solenoidal by a term in ρ without altering the value of $V\rho\tau_1$. Hence we may suppose $S\nabla\tau_1 = 0$, and the right side of (15) cannot vanish if τ_1 does not vanish and n is not -1; that is, the term $V\rho\tau$ is uniquely determined.

6. From the identity (14) may be easily deduced a second example of inverse operation (integration) with ∇. Suppose a rotation vector, $(V\nabla F\rho)$, to be known at all points of a given region, and to be expressible as a sum of vectors each homogeneous in ρ, lacking a term of degree -2. For example, let

$$\text{rotation vector} = V\nabla F\rho = \tau_0 + \tau_1 + \tau_2 + \dots,$$

where the subscripts denote the degrees of their terms. A possible value of $F\rho$ then is

$$F\rho = -V\rho\left\{\frac{\tau_0}{2} + \frac{\tau_1}{3} + \frac{\tau_2}{4} + \dots\right\}, \quad . \quad . \quad (16)$$

a vector everywhere at right angles to ρ. The vector $F\rho$ is often called the vector potential of its derived vector $V\nabla F\rho$. Thus (16) shows how to write down a possible vector potential for any assigned solenoidal vector whose components are either polynomials or other sums of homogeneous terms (exception noted). (16) may be directly verified by expanding the right side with the aid of identities like (15)[†].

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[*] Phil. Mag. *loc. cit.*

[†] It is well known that possible values for a required vector potential can be found by partial integration with respect to the point-coordinates x, y, and z. The above method illustrates how ∇ may replace partial integration,—a principle probably more far-reaching than any application which has yet been made of it. As another illustration, let $Xdx + Ydy + Zdz = d\text{P} = 0$ be an exact differential equation. X, Y, and Z are components of the vector ∇P. Suppose $\text{P} = S\rho F\rho$. If ∇P can be written as a sum of homogeneous vectors

$$\nabla\text{P} = \sigma_0 + \sigma_1 + \sigma_2 + \dots$$

we may write down P by the formula

$$\text{P} = -S\rho\left\{\frac{\sigma_0}{1} + \frac{\sigma_1}{2} + \frac{\sigma_2}{3} + \dots\right\},$$

proved by multiplying both sides of (13) by ρ and taking scalars.

7. Most of the foregoing results are extensions of familiar properties of linear vector functions. The identity (13), expressing a homogeneous vector at the sum of an irrotational vector and a vector perpendicular to ρ, appears in the linear case as the familiar

$$\phi\rho = \omega\rho + \mathrm{V}\epsilon\rho \text{ (Tait, Art. 186)}, \quad . \quad . \quad . \quad (17)$$

where ω is a self-conjugate linear function and ϵ is a constant vector.   Here $\omega\rho = \dfrac{\phi\rho + \phi'\rho}{2}$, and $\mathrm{V}\epsilon\rho = \dfrac{\phi\rho - \phi'\rho}{2}$, whence the identity (17) may be written

$$\phi\rho = \frac{\phi\rho - \phi'\rho}{2} + \frac{\phi\rho + \phi'\rho}{2}. \quad . \quad . \quad . \quad (18)$$

To bring out the analogy between (13) and (18), put, as before, $d\mathrm{F}\rho = \phi d\rho$, so that $\phi\rho = n\mathrm{F}\rho$ by Euler's theorem, and $\nabla\mathrm{S}\rho\mathrm{F}\rho = -\phi'\rho - \mathrm{F}\rho$ by (12). By (2), $\mathrm{V}\rho\mathrm{V}\nabla\mathrm{F}\rho = (\phi' - \phi)\rho$. By substitution of these values, (13) becomes

$$\mathrm{F}\rho = \frac{(\phi - \phi')\rho}{n+1} + \frac{\phi\rho + n\phi'\rho,}{n(n+1)} \quad . \quad . \quad . \quad (19)$$

which evidently reduces to (18) for the case $n=1$. The right-hand term may be taken as an extended $\omega\rho$; and, just as $\omega\rho$ is at all points of space normal to the general family of central quadric surfaces $\mathrm{S}\rho\phi\rho = \text{const.}$, so this term is normal to the cubic or higher surfaces $\mathrm{S}\rho\mathrm{F}\rho = \text{const.}$ Again, just as the axes of $\omega\rho$ possess the special property of being mutually at right angles, so the axes of its analogue have a specific configuration ; but the consideration of axes lies outside the scope of the present paper.

8. The identity (13) also throws a good deal of light on the nature of orthogyral vectors. To distinguish these sharply from other vectors, we may say that an orthogyral vector is one satisfying the two following conditions :—

1. Neither the vector nor its curl vanishes identically.

2. The scalar product of the vector and its curl vanishes identically.

Lamellar vectors are thus excluded from the company of orthogyral vectors. It will also be convenient to distinguish two cases, according as $\mathrm{S}\rho\mathrm{F}\rho$ does, or does not, vanish identically. If an orthogyral vector $\mathrm{F}\rho$ is everywhere at right angles to ρ, the family of surfaces normal to $\mathrm{F}\rho$ consists of cones. The right-hand term of (13) disappears, and the vector may be said to be *conical*. If, on the other hand, $\mathrm{S}\rho\mathrm{F}\rho$ does not

vanish identically, an orthogyral $F\rho$ may be said to be *mixed.*
These two types are clearly not restricted to homogeneous
vectors. I shall speak of the scalar $S\rho F\rho$ as the *associated
scalar* of the vector $F\rho$.

From (13) we may now deduce a variety of simple con-
sequences. First, *any* homogeneous vector whose associated
scalar vanishes identically is orthogyral. This is evident from
the mere form of (13) except when $n = -1$. In this case it
can be shown by actual expansion of $V\nabla V\rho\tau$, as in (15).

Second, if a homogeneous orthogyral vector be divided
by its associated scalar, the resulting vector is lamellar, for we
have

$$V\nabla \left\{ \frac{V\rho V\nabla F\rho + \nabla S\rho F\rho}{S\rho F\rho} \right\} = 0,$$

by actual expansion, if $SF\nabla F = 0$, *i. e.* if F is orthogyral.
Exception must be made of conical vectors.

It further appears from (13) that the theory of orthogyral
vectors may be connected with that of algebraic plane curves.
Suppose n, the degree of the homogeneous vector $F\rho$, to be a
positive integer, and let $F\rho$ be orthogyral of mixed type,
and let its components be polynomials. Let x, y, and z, the
usual coordinates of a point ρ in space, define a point in a
plane in homogeneous coordinates. Then the associated
scalar, $S\rho F\rho$, will define, by its vanishing, a plane curve, of
degree $n + 1$. I shall now show that if $F\rho$ is orthogyral the
curve defined by its associated scalar must have n double
points. The condition that $F\rho$ shall be orthogyral is that
the scalar product of the two vectors $V\nabla F\rho$ and $\nabla S\rho F\rho$
shall vanish identically. Call the components of $\nabla S\rho F\rho$
X, Y, and Z, and those of $V\nabla F\rho$ X_1, Y_1, and Z_1. Expanding
the scalar product we have the condition

$$XX_1 + YY_1 + ZZ_1 = 0, \text{ identically.}$$

These six components define six curves. Wherever X and Y
both vanish, either Z or Z_1 must vanish. But Z_1 meets X
or Y at most in $n(n-1)$ points, the product of their degrees*.
Hence at the remaining $n^2 - n(n-1)$ intersections of X and
Y we must also have Z vanish. That is, $\nabla S\rho F\rho$ vanishes at
n points, and the curve $S\rho F\rho = 0$ has n double points.

For example, let $n = 1$. The associated scalar, being of
the second degree, defines a conic. It must have one double

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* If Z_1, X, and Y happen to have a common factor, we may make a
new choice of our coordinate system. It is easy to complete the formal
proof.

point, hence consists of two straight lines. We may then put

$$S\rho F\rho = S\alpha\rho S\beta\rho,$$

where α and β are constant vectors. Operating by ∇ gives

$$\nabla S\rho F\rho = -\alpha S\beta\rho - \beta S\alpha\rho.$$

The vector $V\nabla F\rho$, being now of degree zero, is constant, and must be parallel to $V\alpha\beta$. Hence the most general orthogyral linear vector is of the form

$$a V\rho V\alpha\beta + b(\alpha S\beta\rho + \beta S\alpha\rho),$$

where a and b are constant scalars.

If we let n equal 2, the associated scalar defines a cubic with two double points, hence degenerate.

If $n=3$, the most general orthogyral vector has for its associated scalar a quartic of deficiency zero.

In a similar manner, if we start with any *two* homogeneous scalars we may write down orthogyral vectors in the form (13). For the vector $V\nabla u\nabla v$ is solenoidal, whatever scalars u and v may be. Hence

$$a V\rho V\nabla u\nabla v + b\nabla(uv)$$

is orthogyral if u and v are homogeneous, a and b being constants. That is, to any pair of algebraic plane curves corresponds a two-parameter family of orthogyral vectors.

9. In conclusion it may be said that the differential and integral relations of this paper are extensions to space of the one-dimensional formulas for $\dfrac{d(x^n)}{dx}$ and $\displaystyle\int x^n dx$. In fact, most of the preceding results reduce to these, or to identities, if we put $\rho = ix$ and $\nabla = i\dfrac{d}{dx}$. That a calculus with ∇ is worthy of systematic and extensive development there can be no doubt. We should naturally expect greater variety and complexity in proportion as the geometry of space is many-sided in comparison with that of one dimension. It would be essential to consider next the values of n treated above as exceptional cases—not a difficult matter, but leading to logarithms and other non-homogeneous functions, beyond the special domain of the present paper.

LXXIV. *Radiation from an Electric Source, and Line Spectra.
The Hydrogen Series.* (*Preliminary Note.*) *By* L. SILBER-
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LET the *source, i. e.* the seat of impressed electric force,
be a sphere, of radius a, having the permittivity K,
while that of the surrounding medium is unity. Then the
intensity of electromagnetic radiation emitted by the source
is, at distances great in comparison with a,

$$J = f(\lambda, K), \quad \ldots \quad \ldots \quad (1)$$

where λ is the wave-length in vacuo and f is a certain
function of λ and $K(\lambda)$ which I will not write out here †.
For large values of K, viz. when the refractive index
$c/v = K^{1/2}$ is of the order 10^3, the spectrum (1) of our
source consists of an infinite series of *very thin and sharp*
" *lines,*" corresponding to the maxima of J, say J_1, J_2, etc.,
arranged after the descending wave-lengths λ_1, λ_2, etc.; the
reciprocals of the latter are the successive roots of a com-
paratively simple transcendental equation. The requirement
that these "lines," or exceedingly narrow bands, should lie
within the visible spectrum, reduces the source to molecular
dimensions ‡. The intensities of the successive spectrum-
lines are, with a high degree of approximation, proportional
to the square of the wave-length, *i. e.*

$$J_1 : J_2 : \ldots = \lambda_1^2 : \lambda_2^2 : \ldots \quad \ldots \quad (2)$$

In other words, *the lines, from red to violet, become fainter and
fainter.*

The permittivity of the source, K, may be, in the general
treatment of the problem, any function of λ, which function
may be said to define the *intrinsic* or *the atomic dispersion.*
In accordance with the essence of the method of investi-
gation employed (*cf. loc. cit.*), I have strictly avoided any
attempt to enter into the mechanism of the "source,"
which may consist of many electrons or other subatomic
entities. Guided by the analogy of molar lumps of matter,
I assume $k \equiv 4\pi^2 a^2 K$ to be, in general, of the form

$$k = \alpha + \sum_{i=1}^{i=\kappa} \frac{\beta_i \lambda^2}{\lambda^2 - \gamma_i^2}, \quad \ldots \quad \ldots \quad (3)$$

* Communicated by the Author.
† This function and the corresponding details of the problem are
given in a paper communicated to the Royal Society, 22nd March, 1915.
‡ The case of small K, corresponding very nearly to the (normal)
continuous spectrum, is treated in the paper quoted above. In that case
a is, at all accessible temperatures, greater than 10^{-5} cm.

where α, β_i, γ_i are constants, which will have to be determined, for each individual spectrum, on the ground of experience, such as the dispersive properties of molar lumps of the substance in question or the characteristic features of the spectrum itself. But we need not enter here upon details of this kind.

The purpose of the present note is shortly to report on certain results already obtained by means of (1) in the simplest case of the dispersion-law (3), viz. for $\kappa = 1$. Then

$$k = \alpha + \frac{\beta}{1 - \gamma^2/\lambda^2}. \quad \ldots \quad \ldots \quad (3\,a)$$

If k_0 be the static value of k, that is, for an invariable impressed force, or for $\lambda/\gamma = \infty$, we have $\alpha + \beta = k_0$. Introducing (3 a) into the full formula (1), I obtain, for the wave-lengths of the successive spectrum-lines,

$$\lambda_i^2 = \frac{1}{2}\left(\gamma^2 + \frac{k_0}{u_i^2}\right) + \left\{\frac{1}{4}\left(\gamma^2 + \frac{k_0}{u_i^2}\right)^2 - \frac{\alpha\gamma^2}{u_i^2}\right\}^{1/2}, \quad . \quad . \quad (4)$$

where u_i ($i = 1, 2, 3, \ldots$) are the successive roots of the transcendental equation mentioned above [*]. The relative intensities of the "lines" are given by (2), and since $K_2 > K_1$, $K_3 > K_2$, etc., the successive lines become not only *fainter* but also *sharper*. The values of the successive roots, u_1, u_2, etc., increase indefinitely, so that the lines become more and more crowded from the red towards the violet end of the spectrum, and, by (4),

$$\lambda_\infty = \gamma. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Thus, the lines constitute a series having its *convergence-point* at $\lambda = \gamma$.

These being exactly the characteristic features of the so-called "first" hydrogen spectrum [†], it seemed interesting to try to determine the constants α, β, γ (and the order of magnitude of K), so as to represent the beautiful series of that gas by the formula (4). My calculations, which now extend over many days, are not yet completed. The following tables contain some of the results of my first attempts. In each of these tables, the first column contains the order-number (i) of the root; the second column, λ_i calculated by means of (4), in microns; the third, the

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[*] Owing to the large values of K_0, and, *a fortiori*, of $K\lambda$, $\lambda \gtreqqless \gamma$, this transcendental equation becomes $\dfrac{K}{u^2} + \dfrac{\cos u}{g(u)} = 0$, where $g(u) = \sin u/u - \cos u$.

[†] Which, in its essence, is also shown by aluminium and thallium.

observed wave-lengths (to five figures only), with the usual
short denominations of the hydrogen lines ; and finally, the
fourth column, the differences, $\Delta = \lambda_{calc.} - \lambda_{obs.}$, in Ångström
units. The symbol λ_B stands for Balmer's "theoretical
end," if we are to translate literally the name used by
Germans. The constants, at the top of each table, are given
in microns. I should like to remark that the tables are
numbered, not according to the importance to be attributed
to the degree of agreement attained, but simply in their
chronological order.

<div align="center">

TABLE I.

$\gamma = \cdot3660_8$; $k_0 = 4\cdot1200$; $\alpha = -3\cdot2398$.

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$i.$	$\lambda_{i\ calc.}$	$\lambda_{obs.}$		Δ
3	$\cdot4336_8$	$\cdot4340_7$	H_γ	$-3\cdot9$
4	$\cdot4097_6$	$\cdot4102_3$	δ	$-4\cdot7$
5	$\cdot3965_2$	$\cdot3970_2$	ϵ	$-5\cdot0$
6	$\cdot3884_4$	$\cdot3889_2$	ζ	$-4\cdot8$
7	$\cdot3831_6$	$\cdot3835_6$	η	$-4\cdot0$
8	$\cdot3795_5$	$\cdot3798_1$	θ	$-2\cdot6$
9	$\cdot3769_5$	$\cdot3770_8$	ι	$-1\cdot3$
10	$\cdot3750_5$	$\cdot3750_3$	κ	$+0\cdot2$
11	$\cdot3735_8$	$\cdot3734_5$	λ	$+1\cdot3$
12	$\cdot3724_5$	$\cdot3722_0$	μ	$+2\cdot5$
13	$\cdot3715_9$	$\cdot3712_1$	ν	$+3\cdot8$
14	$\cdot3708_3$	——		——
15	$\cdot3702_5$	$\cdot3704_0$	ξ	$-1\cdot5$
16	$\cdot3697_6$	$\cdot3697_2$	o	$+0\cdot4$
17	$\cdot3693_6$	——		——
18	$\cdot3690_2$	$\cdot3691_7$	π	$-1\cdot5$
19	$\cdot3687_3$	$\cdot3687_1$	ρ	$+0\cdot2$
20	$\cdot3684_7$	$\cdot3682_9$	σ	$+1\cdot8$
$\vdots$	$\vdots$	$\vdots$		
∞	$\cdot3660_8$	$\cdot3661_2$	H_{31}	$-0\cdot4$
	——	$\cdot3646_1 = \lambda_B$		

It will be noticed that the theoretical "lines" λ_{14} and λ_{17}
are superabundant * ; such would be also λ_{21} ; λ_{22} coincides

* The first of these may also be coordinated with H_ξ, giving
$\Delta = +4\cdot3$.

nearly with H_r, *i. e.* with H_{21} (Balmer's $m=21$; H_a is H_3), λ_{28} with H_{23}, and λ_∞ very nearly with H_{31}, the last observed line of the hydrogen series. In a word, from $i=20$ or so the formula (4) is "getting out of step," with the above constants that is. The reason of the superabundance of theoretical lines is, of course, the choice of γ just behind the last observed line H_{31}, which is certainly before the convergence-point of the series (15·1 Å.U. before λ_B). Owing to this circumstance the theoretical lines begin to crowd, as it were, too early. This is one defect of Table I. Another, more serious, defect is that the above constants γ, α, k_0 give, for $i=1$ and $i=2$,

$$\lambda_1 = \cdot6267, \quad \lambda_2 = \cdot4839,$$

whereas the first two hydrogen lines are (to four figures)

$$H_a = \cdot6563, \quad H_\beta = \cdot4861,$$

so that the corresponding differences are $\Delta = -296$ (!) and -22 Å.U. They have, therefore, not been incorporated into Table I. In fact, the constants used in that table have been calculated without any regard to H_a, H_β. (And i the reader tries to determine α and k_0 from these two rebellious lines, so as to make them fit exactly, or nearly so, he will at once spoil the rest of the series, from λ_3 till the end.) But apart from these two defects, the agreement of the two columns of Table I., and more especially for $i=3$ till $i=13$ *, seems remarkable. Notice that the decreasing intensities of the successive lines, as expressed by (2), and not given in the table, may serve as a supplementary corroboration of the formulæ here proposed.

In Table II., in which γ is very little smaller than in the preceding table, the constants k_0, α have been determined from postulating $\lambda_4 = H_\delta$, $\lambda_5 = H_\epsilon$. Hence the absence of Δ for these two lines, calculated only for the sake of control. But the exceedingly close agreement of λ_6, λ_7, λ_8, λ_9 with H_ζ, etc., seems very remarkable. The results for λ_1, λ_2 are as bad as in the first case, but the agreement for the remaining part of the series is, in general, more close.

The coordination of the theoretical and observed λ's

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* The lines being here less crowded than in the lower part of the table, there is little probability for the agreement being a "chance-agreement."

TABLE II.

$$\gamma = \cdot 3660_6 \; ; \quad k_0 = 3\cdot 5345 \; ; \quad \alpha = -4\cdot 0819.$$

$i.$	$\lambda_{i\,\text{calc.}}$	$\lambda_{\text{obs.}}$		Δ
3	$\cdot 4338_1$	$\cdot 4340_7$	H_γ	$-2\cdot 6$
4	$\cdot 4102_3$	$\cdot 4102_3$	δ	$0\cdot 0$
5	$\cdot 3970_2$	$\cdot 3970_2$	ϵ	$0\cdot 0$
6	$\cdot 3888_9$	$\cdot 3889_2$	ζ	$-0\cdot 3$
7	$\cdot 3835_5$	$\cdot 3835_6$	η	$-0\cdot 1$
8	$\cdot 3798_6$	$\cdot 3798_1$	θ	$+0\cdot 5$
9	$\cdot 3772_3$	$\cdot 3770_8$	ι	$+1\cdot 5$
10	$\cdot 3752_7$	$\cdot 3750_2$	κ	$+2\cdot 5$
11	$\cdot 3737_9$	$\cdot 3734_5$	λ	$+3\cdot 4$
12	$\cdot 3726_2$	$\cdot 3722_0$	μ	$+4\cdot 2$
13	$\cdot 3717_3$	$\cdot 3712_1$	ν	$+5\cdot 2$
14	$\cdot 3709_7$	$\cdot 3704_0$	ξ	$+5\cdot 7$
$\vdots$	$\vdots$	$\vdots$	$\vdots$	
∞	$\cdot 3660_6$	$\cdot 3661_2$	H_{31}	$-0\cdot 6$
		$\cdot 3646_1 = \lambda_B$		

becomes, after $i = 13$ or 14, ambiguous. There are again superabundant lines, owing to the smallness of the interval $\lambda_\infty - H_{31}$. Compare the remarks made above. To prevent the premature crowding of the theoretical lines and to take in, at the same time, the hitherto ignored lines H_a, H_β, the convergence-point $\lambda_\infty = \gamma$ is pushed back, nearly as far as Balmer's limit. Some of the results of the corresponding calculation, which is just started and is being assiduously retouched (with regard to the values of α, k_0), are collected in Table III. Its chief purpose here is to show that the enormous value of Δ for H_a can well be reduced, although at the price of spoiling to a certain extent the successive lines, and that the superfluous theoretical lines can be entirely abolished. It will be enough to give here the wave-lengths to four figures only.

The numbers (1), (2), etc. inserted in the third column stand for "first, second, etc." observed line of the hydrogen series; they may facilitate the testing of coordination. It is quite possible that the simplest dispersion formula $(3a)$ will turn out to be too narrow for the purpose of reducing

TABLE III.

$$\gamma = \cdot3649_3 \; ; \quad k_0 = 5\cdot0500 \; ; \quad a = -2\cdot5000.$$

$i.$	$\lambda_{i\,calc.}$	$\lambda_{obs.}$		Δ
1	·6499	(1) ·6563	H_α	−64
2	·4909	(2) ·4861	β	+48
3	·4363	(3) ·4341	γ	+22
4	·4107	(4) ·4102	δ	+ 5
6	·3881	(6) ·3889	ζ	− 8
8	·3789	(8) ·3798	θ	− 9
12	·3715	(12) ·3722	μ	− 7
16	·3687	(16) ·3692	π	− 5
21	·3672	(21) ·3674	ϕ	− 2
28	·3662$_2$	(28) ·3662$_1$ H_{30}		+ 0·1
29	·3661$_3$	(29) ·3661$_2$ H_{31}		+ 0·1
⋮ ∞	⋮ ·3649$_3$	$\lambda_B = \cdot3646_1$		+ 3·2

the greatest Δ of Table III. to one or a few Å.U. only ; but before deciding on the introduction of two new constants, by using formula (3) with $\kappa = 2$, I shall not spare further efforts to succeed with the simpler dispersion law $(3\,a)$. The results of my further calculations, together with some general consequences of the proposed theory, will be reported in a later publication.

London, April 8, 1915.

LXXV. *An Atomic Model with a Magnetic Core. By* H. Stanley Allen, *M.A., D.Sc., Senior Lecturer in Physics at University of London, King's College* *.

IN spite of their limitations models have been of great service in the development of physical theories. The two models illustrating the structure of the atom that have attracted most attention are those that have been suggested by Sir J. J. Thomson and Sir E. Rutherford respectively. Thomson's atom consists of a sphere containing a uniform volume distribution of positive electricity, in which a certain number of negatively electrified corpuscles are distributed. In Rutherford's atom there is a central

* Communicated by the Author.

nucleus of small dimensions carrying a positive charge, and this nucleus is surrounded by electrons in orbital motion. According to Nicholson coplanar rings of electrons are not possible in such a case, and the model can neither be of the "planetary" nor of the "Saturnian" type; but, provided the electrons are in one plane, can only possess a single ring of electrons.

In these models only the electrostatic forces due to the positively charged portion of the atom are taken into account. It has been pointed out by the present writer[*] that it may be necessary to consider not only electrostatic but also magnetic forces in the immediate vicinity of the atom. According to this view the atom would consist of a magnetic core which is electrically charged, surrounded by electrons in orbital motion. Whether it is possible for the electrons to form concentric rings in this case is a point deserving the attention of mathematicians; experimentally such rings appear to have sufficient stability to allow them to be directly observed as in the striking cases recorded by Birkeland[†]. In these experiments photographs were taken of the discharge through a large vacuum-tube with a magnetized sphere as cathode. Rings were formed round this globe resembling the rings of Saturn, in some cases as many as three distinct rings could be observed.

The Scattering of the Alpha Rays.

The scattering of alpha rays by atoms of matter has afforded results from which Rutherford has formed an estimate of the size of the nucleus. In the theory of scattering which he has proposed only electrostatic forces are considered. In this case the scattering depends on the inverse fourth power of the velocity of the α particle. If we consider an α particle moving in the equatorial plane of a simple magnet, it appears that the scattering would depend on the inverse square of the velocity. In the general case of a charged particle projected in any direction in a combined magnetic and electrostatic field, it is probable that some intermediate law would be obeyed. The experiments of Geiger and Marsden[‡] agree moderately well with the

[*] 'Nature,' vol. xcii. p. 630 (1914).
[†] Birkeland, *C. R.* vol. cliii. p. 938 (1911).
[‡] Geiger & Marsden, Phil. Mag. vol. xxv. p. 620 (1913). "Several experiments were made, and in every case the scattering was found to vary at a rate more nearly proportional to the inverse fourth power of the velocity than to any other integral power. Owing to the comparative uncertainty of the values of the velocity for small ranges, however, the error of experiment may be somewhat greater than appears from column V. of the table." The tabulated numbers vary from 22 to 28.

first law, but the point is one of so much importance that it may repay further examination.

The scattering of α rays by the magneton has been discussed by Hicks[*], who has calculated a number of trajectories in the equatorial plane similar in character to those investigated by Størmer[†]. The difficulty of forming an estimate of the amount of scattering is very considerably increased in the general case when the α particle is projected towards a magnetic atom in any direction whatever, but the results obtained by Hicks go to show that scattering of the right order of magnitude can be obtained by postulating a reasonable number of magnetons in the core.

There is no idea of calling in question the mathematical investigations of C. G. Darwin[‡], who dealt with the motion of a charged particle under the action of a central force varying as some power of the distance. The only question at issue is whether the experimental results on scattering are of so decisive a character as to prohibit the introduction of magnetic forces, and to lead with certainty to the conclusion that the nucleus of a heavy atom cannot have a radius much exceeding 10^{-13} cm.

The Size of the Nucleus.

Two arguments only have been advanced in favour of the extremely small diameter assigned to the nucleus of the Rutherford atom. The first is derived from the wide-angle scattering of α particles, and, as we have seen, the argument is inconclusive because no account has been taken of the possibility of a magnetic field being associated with the atom. The second depends on the assumptions that the whole mass of the nucleus is electromagnetic in origin and that this mass arises from a structureless charge of magnitude Ne, where N is the atomic number. Now we know that both α and β particles are derived from the nucleus of radioactive substances, and it is hardly thinkable that these should exist in the nucleus save as discrete particles. We conclude that at least for the elements of high atomic weight the nucleus must possess a structure, though it remains to some extent doubtful whether the two elements, hydrogen and helium, at the beginning of the periodic table, are to be looked upon as possessing a *simple* or a *complex* nucleus. According to the views advanced by Nicholson from a study

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[*] W. M. Hicks, Proc. Roy. Soc. vol. xc. p. 356 (1914).

[†] Størmer, *Archiv for Mathematik*, Christiania, vol. xxviii. p. 36 (1906).

[‡] C. G. Darwin, Phil. Mag. vol. xxv. pp. 201–210 (1913).

of nebular and coronal spectra, the nucleus for each of these elements is probably complex. It is only to the simple nucleus that we need attribute the small size necessary to account for the large mass.

The properties of a terrestrial element connected with its atomic number N can be explained just as in the case of the Rutherford atom, if the resultant positive charge of the complex nucleus amount to Ne. In particular Bohr's theory of the hydrogen spectrum remains unaffected if we attribute a complex character to the nucleus, provided the resultant positive charge of the nucleus be $+e$.

The interesting results obtained by Nicholson in his paper on Electromagnetic Inertia and Atomic Weight [*] appear to the writer to indicate a diameter for the nucleus of an atom of radium or of thorium considerably greater than that formerly assigned. Thus it is suggested in the paper that the α particles in a thorium atom have a mean distance apart comparable with the radius of an electron, 10^{-13} cm. Now as the atom of thorium must contain the equivalent of about 58 α particles, it would appear that the radius of the complex nucleus of thorium must be considerably greater than 10^{-13} cm.

The view to which we are thus led is that the central portion of an ordinary atom may contain α and β particles, or hydrogen nuclei in orbital motion. This motion would give rise to an external magnetic field. But as the velocities in question must presumably be less than that of light, the radius of the *magnetic core* must be greater than that of the simple nucleus of Rutherford, and is perhaps of the order of 10^{-10} cm.

Magnetism.

The views of magnetism that are widely accepted at the present time are those developed by Langevin and by Weiss. An electron in orbital motion may be regarded as equivalent to an elementary magnet. According to the theory of Weiss there is a certain elementary magnet, the magneton, which is common to the atom of a large number of different substances. It was pointed out in a discussion on this theory at a meeting of the German Naturforscherversammlung in 1911, that there may be a connexion between Planck's "universal constant" h and the magnetic moment of the magneton. Nicholson regards this constant as an angular momentum. McLaren [†] identifies the natural unit of

* Nicholson, Phys. Soc. Lond. Feb. 26, 1915.
† McLaren, 'Nature,' vol. xcii. p. 165 (1913).

angular momentum with the angular momentum of the magneton. According to Bohr's theory [*] the angular momentum of a "bound" electron is constant and is $h/2\pi$. Conway [†], using a different model, obtains the value h/π. Let us suppose that an electron (charge e, mass m) is moving in a circular orbit (radius a) with angular velocity ω. Then its angular momentum is $ma^2\omega$, and the magnetic moment of the equivalent simple magnet is $\frac{1}{2}ea^2\omega$. Thus the magnetic moment is equal to some constant multiplied by he/m. Taking the angular momentum as $h/2\pi$, we obtain

$$\frac{h}{4\pi}\frac{e}{m} = 92\cdot7 \times 10^{-22} \text{ E.M.U.}$$ as the value of the magnetic

moment. This is *exactly* 5 times the magnetic moment of the magneton of Weiss. This numerical relation was first pointed out by Mr. Chalmers [‡] at the discussion on Radiation at the Birmingham meeting of the British Association. The magnetic moment of the magneton is found by dividing the magnetic moment of the atom gram $1123\cdot5$ by Avogadro's constant. Weiss used the value of this constant found by Perrin, but if we take the more recent value given by Millikan ($60\cdot62 \times 10^{22}$) we obtain as the magnetic moment of the magneton $18\cdot54 \times 10^{-22}$, which is exactly 1/5 of the number given above.

These commensurable numbers may be of significance in connexion with the structure of the atom. The magneton may arise as a difference effect. The way in which this may come about may be illustrated by a simple model. Suppose we have a uniform sphere of positive electrification of radius A rotating in the same sense as an electron with angular velocity Ω. Outside this, suppose we have a single ring of mean radius a containing n electrons. The remaining negative electrification required to produce a neutral system may be supposed concentrated at the centre without rotation. Then the magnetic moment of the rotating sphere § may be

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[*] Bohr, Phil. Mag. vol. xxvi. p. 1, p. 476 (1913).

[†] Conway, Phil. Mag. vol. xxvi. p. 1010 (1913).

[‡] See 'Nature,' vol. xcii. pp. 630, 687, 713 (1914). The same relation was noticed independently by Dr. Bohr (Richardson, 'The Electron Theory of Matter,' p. 395).

§ This is a particular case of a more general theorem. Since the magnetic moment arising from a charge e moving in a circular orbit of radius a with angular velocity ω is $\frac{1}{2}ea^2\omega$, the magnetic moment arising from a volume distribution of electricity rotating about an axis is $\frac{1}{2}\Sigma\rho\,dv\,r^2\Omega$, where ρ is the electrical density and dv an element of volume. Assuming ρ constant, the magnetic moment

$$\begin{aligned} &= \tfrac{1}{2}\rho\Omega\Sigma r^2 dv \\ &= \tfrac{1}{2}\rho\Omega V k^2 \\ &= \tfrac{1}{2}E k^2 \Omega, \end{aligned}$$

taken as $\frac{1}{5}EA^2\Omega$, where E is the total positive charge, which we shall assume equal to Ne. We have no direct evidence as to the value of $A^2\Omega$, but if, for convenience, we assume that it has the same value as $a^2\omega$ for an electron in the ring, the magnetic moment of the rotating core becomes $\frac{1}{5}Nea^2\omega$. But a magnetic moment of $\frac{1}{2}ea^2\omega$ is equivalent to 5 magnetons. Consequently the magnetic moment of the core is equivalent to 2N magnetons. The resultant magnetic moment for the atomic model would be the difference between the 2N magnetons of the core and the 5n magnetons of the ring. Thus the magneton may be introduced as a unit for measuring magnetic moments without necessitating the existence of a single magneton as an independent entity.

It is not intended that this model should do more than serve as a crude illustration of the structure of an atom, for there can now be little doubt as to the complex character of the core at least in the case of the heavier elements. In particular a spherical or spheroidal distribution is not an essential feature of the proposed atomic model. It may be that all parts of the core must move in one plane. There are obvious outstanding difficulties such as the way in which the parts of the core hold together so as to form a stable system. Passing over these difficulties, the resultant magnetic moment of the atom with a spherical core would be either the sum or the difference of 2N and 5n magnetons, according to the relative directions of rotation of the core and the ring.

It would seem that the diamagnetic properties of such an atom would depend mainly on the ring, if a is much larger than A. For the expression for the magnetic susceptibility would consist of a series of terms of which the most important would be $k = -\dfrac{ne^2a^2}{4m}$.

Pascal [*] has shown that the molecular susceptibility of a large number of chemical compounds can be calculated by

where V is the total volume, k the radius of gyration for a uniform distribution of mass, and E the total charge of the rotating system.

Thus both for a sphere and for a spheroid rotating about an axis of symmetry, the magnetic moment is $\frac{1}{5}EA^2\Omega$.

We may note here that if the electrical distribution is associated with a proportional distribution of mass, the total mass being $\mathfrak{M}$, the angular momentum is $\mathfrak{M}k^2\Omega$. If we assume that this is a multiple of $h/2\pi$, say $\tau h/2\pi$, the magnetic moment may be written $\dfrac{E}{\mathfrak{M}} \times \dfrac{\tau h}{4\pi}$.

* Pascal, *C. R.* vol. clii. pp. 862–865, 1010–1012 (1911).

adding together the appropriate multiples of the atomic susceptibilities and a constant term depending on the structure of the molecule. Further, he has shown that the elements chlorine, bromine, iodine, and fluorine (and some others) contain a common aliquot part in the specific susceptibility. Certain compounds of the halogens show less susceptibility than would be expected from the additive law. This *diminution* can be expressed in terms of the same aliquot part, whose value is $0\cdot2468 \times 10^{-7}$. If we identify this quantity with the effect of a single electron in the ring, we are led to the conclusion that the radius of the ring is about the same for the elements in question, and that its value is of the order of magnitude to be expected.

The difficulties connected with the explanation of paramagnetic properties are, of course, left untouched by these suggestions. No one has as yet explained how the orbits become tilted when under the influence of an external magnetic field. We may note that a similar difficulty is found in connexion with Ritz's theory of the Zeeman effect, which is attributed to a precessional motion of the elementary magnet, no explanation being forthcoming of the way in which the precessional motion is set up.

The Quantum Theory of Spectral Series.

The success of Bohr's theory in explaining the ordinary Balmer's series in the spectrum of hydrogen, and especially in obtaining close agreement between the observed and the calculated values of Rydberg's constant, raises a strong presumption in its favour. The essential feature of the theory is the emission of exactly one quantum of energy as monochromatic radiation in the passage between one steady state of motion and another. This leads directly to an expression for the frequency, ν, as the difference between two " sequences," the form of the expression being

$$\nu = \frac{\nu_0}{D_2{}^2} - \frac{\nu_0}{D_1{}^2}.$$

When, however, an attempt is made to apply the theory to the spectral series of elements other than hydrogen, serious difficulties are encountered. These have been discussed by Nicholson [*] with special reference to the spectra of helium and of lithium. In the first place, it is necessary to suppose that every electron concerned in the emission of radiation emits one quantum, instead of supposing that one quantum

* Phil. Mag. vol. xxvii. pp. 541-5(4, vol. xxviii. pp. £0-103 (1914).

only is emitted in passing from one state to another. This is required both for ordinary spectra and for X-ray spectra. In the second place, it appears necessary to assume that there is no force between bound electrons, so that any one of these electrons is independent of the others. This supposition may be related to Sir J. J. Thomson's conception of tubes of force. A bound electron may have the tube (or tubes) of force originating from it attached to the nucleus, and if all the electrons in question are connected to the nucleus in this way, they cannot exert force on one another.

Perhaps it may be necessary to suppose that a bound electron has both the ends of the double tube of force belonging to it attached to a definite part of the core in such a way that the attraction on the electron is proportional to e^2 instead of to $(Ne)^2$.

A further difficulty in applying the theory of Bohr to actual series lies in the fact that the denominator of a sequence contains terms which are not simple integers. Thus in Rydberg's formula we have $m + \mu$ where m is an integer, μ a fraction, in the formula of Moggendorf and Hicks we have $m + \mu + \alpha/m$, in the formula of Ritz $m + \mu + \beta/m^2$. Nicholson [*] has shown that the theory in its original form is insufficient to account for such additional terms when electrostatic forces only are considered. The development which I have given [†], supposing the electron to be under the action of magnetic forces, yields a formula containing a term of the form B/m^2, where B is proportional to the magnetic moment of the core, but does not account for the fractional part μ. In attempting to apply this formula to actual elements, it is found that in general the value of β obtained by Ritz is much too large to be due to a small number of magnetons. Further, in the case of hydrogen, if we suppose the fractional part due to a term of the form B/m^2, it is necessary to assume different values for B in the two sequences, implying the existence of two types of state in the core. This suggested that the core itself might be intimately concerned in the emission of radiation, and that the term in μ, and perhaps also terms such as α/m and β/m^2, might depend upon the angular momentum of the core.

This line of thought, associating the constants in the formula with the core of the atom, may be supported by

* *Loc. cit.*
† Phil. Mag. vol. xxix. pp. 40–49, 140–143 (1915).

several recorded results.   According to Hicks [*] both μ and α depend on the atomic weight or atomic volume of the element, α/μ being a pure number and equal to 0.21520. Birge [†] points out that the coefficients in the formula of Ritz increase with increasing atomic weight, being proportional to the atomic volume in the case of sodium, potassium, rubidium, and cæsium.

Several investigators have drawn attention to relations between frequencies and atomic weights, Ramage and Marshall Watts in particular having obtained relationships involving the square of the atomic weight.   This of course implies that the constants in the spectral formulæ depend upon the atomic weight of the element in question.

Hicks finds that the change necessary in the value of μ to account for the observed differences in the frequencies of doublets and triplets can be expressed in terms of a quantity which he calls the 'oun' depending on the square of the atomic weight.

Further arguments may be drawn from the " combination principle of Ritz."   The formula of Ritz may be written

$$n = A - \frac{N}{[m + \mu + \beta(A-n)]^2},$$

which is usually abbreviated as

$$n = A - (m, \mu, \beta).$$

The values of μ and of β differ in different " sequences," and Ritz shows that frequencies corresponding to definite lines can be obtained by taking the difference between various sequences.

In the case of a principal sequence μ may have two values μ_1 and μ_2, the corresponding values of β being β_1 and β_2. Ritz proves that other lines may be obtained by taking $(m, \mu_1 - \mu_2, \beta_1 - \beta_2)$ as a sequence.   In the case of the triplets of the alkaline earths, differences such as $\beta_1 - \beta_2$ for the principal series are the same as the corresponding differences calculated from the diffuse series, so that evidence of a new combination exists here.

According to the simple form of the theory put forward in my former paper, β is proportional to the magnetic moment of the core.   From this point of view, it is not difficult to understand how we can get combinations such as $\beta_1 - \beta_2$, regarding the core as composed of positively and negatively electrified particles in orbital motion.

    [*] Hicks, Phil. Trans. vol. ccx. p. 85 (1910) ; vol. ccxii. p. 33 (1912); vol. ccxiii. p. 323 (1913).
    [†] Birge, Astrophys. Journ. vol. xxxii. p. 112 (1910).

But the significant point is that accompanying $\beta_1 - \beta_2$, we have $\mu_1 - \mu_2$, suggesting that the quantity μ also depends on the revolution of parts of the core in such a way that the effects can be combined by simple addition or subtraction.

For this to be the case, μ would have to be proportional to the first power of the angular velocity, *i.e.* to the angular momentum or to the magnetic moment of the part of the core with which it is associated. Thus it should be possible to express μ in terms of the magnetic moment, and it might be possible to obtain some relation between μ and β.

Rydberg has suggested that the correct expression for the frequency of a line in a spectral series is some function of $\tau + \mu$, where τ is an integer and μ is fractional. This view has received strong support from Thiele, who maintained that the wave-length was some function of $(\tau + \mu)^2$, where τ could take all integral values, both positive and negative. Nicholson's recent critical investigation of the spectrum of helium shows conclusively that in this case the frequency is a function of $\tau + \mu$.

In Bohr's theory of the hydrogen spectrum, the angular momentum of a bound electron is assumed to be constant and equal to $\tau h/2\pi$. In order to obtain a theory applicable to the spectra of other elements, it appears necessary to assume that the angular momentum of the electron is $(\tau + \mu)h/2\pi$. In order to account for the presence of μ in this expression, we assume that we must include with the angular momentum of the electron that of the core, or more probably that of the part of the core which is specially related to the electron. Thus we make the *total* angular momentum of the electron and the part of the core equal to $\tau h/2\pi$.

Then $mr^2\omega \mp I\Omega = \tau h/2\pi.$

So $mr^2\omega = \tau h/2\pi \pm I\Omega$
                       $= (\tau \pm \mu)h/2\pi,$

where $\mu = 2\pi I\Omega/h.$

Proceeding on the lines of Bohr's theory we can then obtain Rydberg's equation.

The extension of the principle of the constancy of angular momentum from the electron to the core, receives a measure of support from the work of Bjerrum and others. Bjerrum assumed that the energy or the momentum of a rotating molecule could be expressed in terms of h. The experimental results obtained from the absorption of infra-red radiation by gases are in agreement with the results of his theory.

The supposition that μ corresponds to the angular momentum of only a part of the core was suggested by the numerical values found in spectral series. It is intelligible

from the point of view of tubes of force, for we may suppose that a tube of force with one end on the electron has the other end attached to a certain part of the core which carries an equal charge of opposite sign. The suggested arrangement appears to be in partial agreement with the views of Stark with regard to the structure of the atom.

In order to secure agreement with known facts as to spectral series it is necessary to regard μ as constant for one type of state of motion, but as possessing different values corresponding to the different types of state.

It cannot, of course, be claimed that these suggestions constitute a theory of spectral series, but an attempt has been made to see what modifications may be required in the original assumptions of Bohr in order to obtain a formula such as that of Rydberg for elements other than hydrogen. The introduction of the coefficient μ renders the structure of the atom somewhat indefinite, for μ depends on (at least two) factors both at present unknown. It may, however, be possible from a study of the numerical values of this quantity in the case of particular elements, or elements belonging to the same chemical group, to throw further light on the character of these factors.

Conclusion.

The atomic model which is suggested in the foregoing pages consists of a ring or rings of electrons surrounding a central core, having a radius considerably greater than the nucleus of the Rutherford atom and in consequence capable of producing appreciable magnetic forces in its vicinity. The total charge of the core must be equal to Ne, where N is the atomic number. The magnetic moment of the core arises from the orbital motion of the discrete electrified particles (α particles, β particles, hydrogen nuclei or positive electrons) of which it is composed. The diamagnetic properties of the atom arise mainly from the external electrons revolving in orbits whose radius is of the order 10^{-8} cm. The magneton is regarded not as an independent entity, but as a unit convenient for measuring magnetic moments introduced in consequence of the principle of the constancy of angular momentum.

A consideration of the laws of spectral series suggests that the quantity μ, the 'phase' of the series, is connected with the angular momentum of the particular part of the core specially associated with the external electron concerned in radiation. A further study of the values of this quantity may lead to a more complete knowledge of the structure of the core.

LXXVI. *The Absorption of Homogeneous β Rays.*
By R. W. VARDER, *M.A. (Cape)* *.

THE experiments described in this paper were made to
investigate as accurately as possible the form of the
ionization absorption curve when very homogeneous β rays
pass through a standard substance like aluminium, and also
to test whether there is any simple relation connecting the
absorption with either the velocity or energy of the β
particle.

The apparatus used is shown in fig. 1.

Fig. 1.
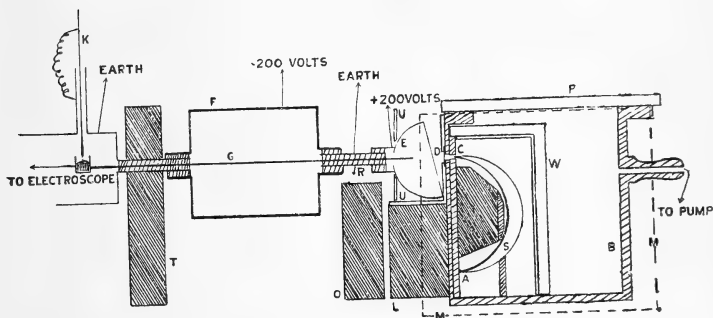
B is a brass box about 3 cm. wide and 10 cm. high. It
was placed between the poles (17 × 10 cm.) of a large electro-
magnet. The position of the pole-pieces is denoted by the
broken line MM. Rays from a thin-walled tube A filled with
radium emanation describe circles in the magnetic field ; a
pencil of homogeneous β rays passing through the slit S
could be concentrated at C. The possibility of obtaining very
homogeneous β rays by this method has been shown by
Rutherford and Robinson †, who employed it to determine
the β ray spectrum of radium B and C. In the present
experiments the relative positions of the source A, the slit S,
and the opening C were arranged to obtain a concentrated
and nearly homogeneous beam at C. The rays there passed
through a rectangular slit 1 cm. × 2 mm. in a brass plate
and through the mica window D. A ground-glass plate P
placed on the top of the box made it airtight. In order to
prevent scattering and diminution in intensity, the air-
pressure in B was reduced to about 1 cm. of mercury. The
window D had a stopping power corresponding to about
2 cm. of air at N.T.P. In this way a strong pencil of β rays

* Communicated by Sir E. Rutherford, F.R.S.
† Rutherford and Robinson, Phil. Mag. Oct. 1913.

was obtained for which the average value of Hρ, where H is the magnetic field and ρ the radius of curvature, could be accurately determined. The value of ρ was fixed at 3·19 cm. in all the experiments, and readings could be obtained up to about Hρ=12,000 gauss cm. From the dimensions of the source, slit, and opening, it was calculated that the variation of Hρ for the issuing rays was less than 3 per cent.

The lead blocks L helped to screen the ionization apparatus from the effects of the γ rays. E is a hemispherical chamber of 2 cm. radius made of coarse copper gauze covered with copper leaf and thin tissue-paper. This vessel was charged to +200 volt. F is a brass cylindrical vessel charged to −200 volt. A copper electrode G passed through two ebonite plugs at the ends of F and terminated at one end in E. The other end of G was connected to a Wilson-Kaye electroscope, which was screened by the lead block T. K is a key for earthing G, and R a guard-ring. A wooden frame W, coated on the inside with celluloid, minimised the effect of reflected β radiation. The vessel F was put in to balance partly the γ ray ionization in E. By altering the position of the lead block O relative to the vessel F, the γ ray ionization in F could be varied so as to neutralize nearly the γ ray ionization in E. Pieces of celluloid U were placed in front, below, and at the back of E as shown. This was done to minimise the reflexion effects of the β rays.

The magnetic fields were measured by comparing the throws of a ballistic galvanometer when an exploring coil was removed from the field, with the throw produced when a known current was broken in the primary of a standard mutual induction. The current in the primary of the mutual induction was measured on a standardized ammeter, and the coils used had also been standardized in some previous work. In this way the fields were measured to about one part in 400. By means of a fluxmeter it was found that the fields were practically uniform over the region traversed by the rays in the box. A given field could always be reproduced by setting the current in the magnet-coils to a certain value and reversing it a number of times.

In taking a reading, the current through the magnet-coils was set at a particular value and reversed a number of times to reach a cyclic state. The vessel B was exhausted by means of a Fleuss pump. The block O was adjusted so that the motion of the electroscope-leaf was slow when a thick aluminium plate was placed over the flat face of E. Readings were taken of the rate of motion of the electroscope-leaf

when various thicknesses of foil were placed over E. The current was then reversed so that no β rays passed through C, and similar readings were taken. A curve of the type AA (fig. 2) was obtained when the field was direct, and one of type BB when the field was reversed; the two curves

Fig. 2.
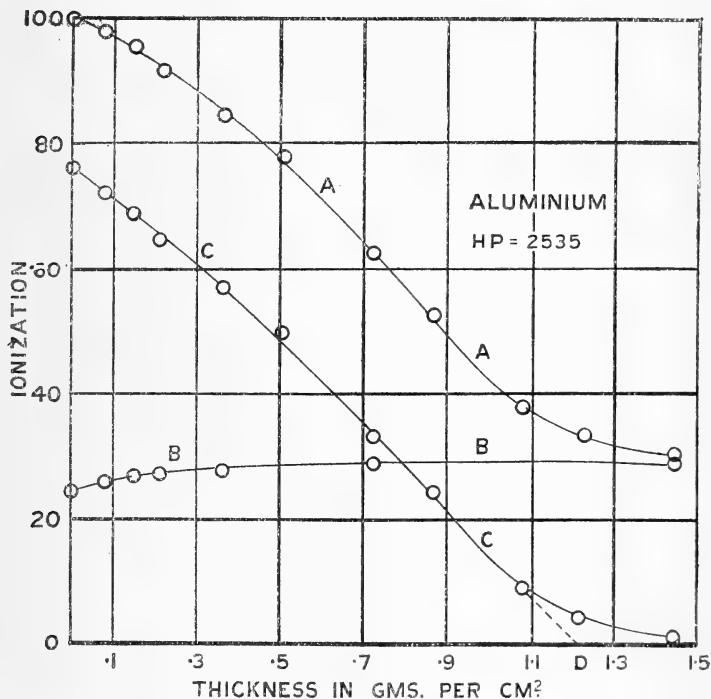
coincided for a very thick absorbing screen. The curve AA represents the combined β and γ ray effect in E, the curve BB represents the γ-ray effect alone, so that the curve CC, which is obtained by subtracting curve BB from the curve AA, represents the curve of β ray absorption. The interpretation of the curve BB will be discussed later.

After a small thickness of matter had been traversed, an approximately linear relation (see curve CC) was found to exist between the ionization and the thickness of the absorbing screen. The curves CC for various velocities are shown in figs. 3 and 4.

The initial drop of the curves varied with the velocity ; this is very probably due to the partial absorption of some of the rays at the edges of the opening C (fig. 1). After this initial drop, the curves are similar in type. In the diagrams the thickness of aluminium is expressed in grams per sq. cm. This thickness in the diagrams is uncorrected for the thickness of the mica window D. The initial rise of the curve BB (fig. 2) is due to β radiation excited in the screens under the conditions of the experiment by the γ rays from A. The current

Fig. 3.
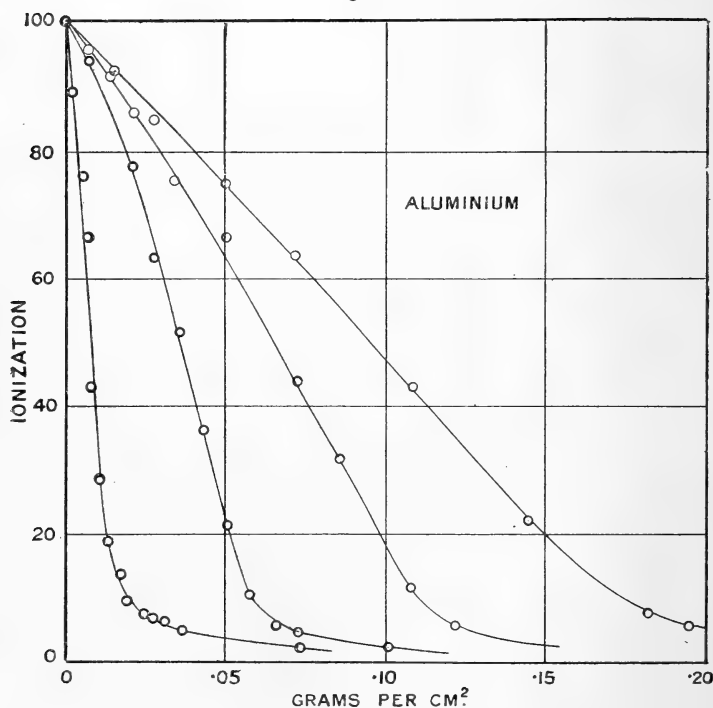
increased with the thickness of the absorbing screens fairly rapidly at first and then very slowly. This effect is very important when the ratio of the β-ray ionization in E to the γ-ray ionization is small. In the experiment with $H\rho = 2000$ gauss cm.—the strong part of the spectrum—this ratio was about 2. In this way absorption curves were taken from

Hρ=1380 to Hρ=11500 gauss cm.   Curves for slower rays
are shown in fig. 3, and for faster rays in fig. 4. β particles
could, however, be detected with certainty up to Hρ=16000,
when they were so swift as to be able to pass through more
than 1 cm. of aluminium.   Readings at this point were
inconvenient on account of the high currents in the magnet-
coils necessary to produce the required field.

Fig. 4.
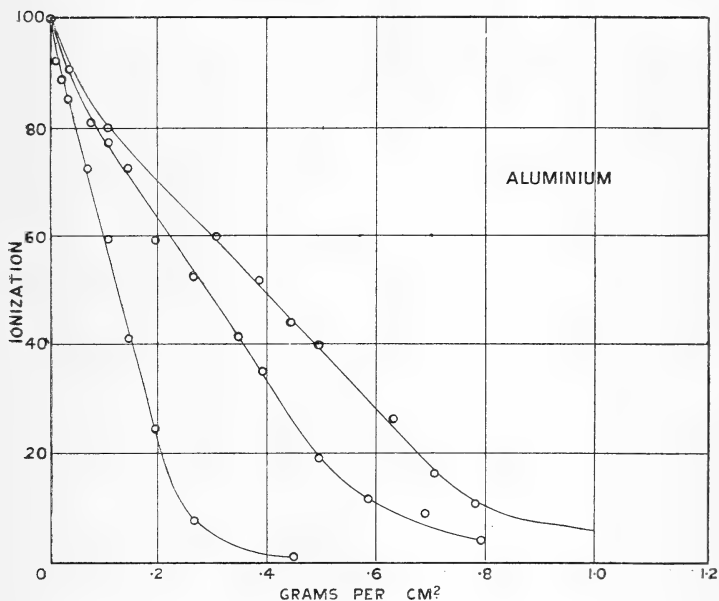
By producing the linear part of curve CC (fig. 2) to cut
the axis of D, we get the thickness of matter, OD, which
would be traversed by the β particles if the law of absorption
had continued as in the linear part of the curve.   The
distance OD might, on analogy of the Bragg α-ray curves,
be called the "range" of the β particle in aluminium.   It
gives the thickness of aluminium in which most of the
β particles are stopped.   Such a quantity may prove useful
in some experiments in deducing the velocity of β rays
from absorption curves.   A curve showing the range of
β rays in aluminium at various velocities is given in
fig. 5.

In discussing this question with Dr. Bohr, he informed me that he had deduced from theoretical considerations that the

Fig. 5.
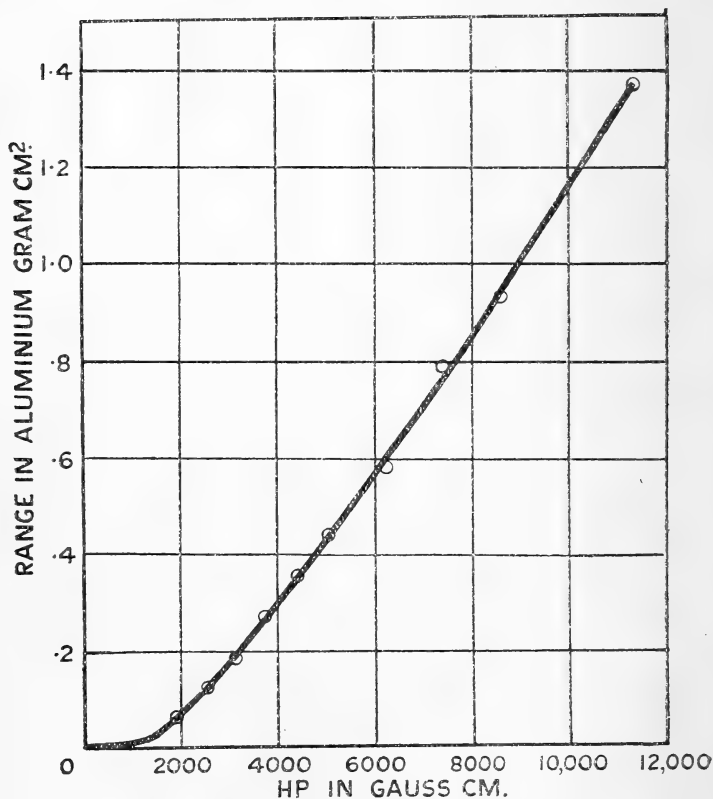
loss of energy (dT) of a β particle in going through a thickness of matter (dx) should be given by

$$\frac{d\mathrm{T}}{dx} = -\frac{\mathrm{K}}{\beta^2},$$

where

$$\mathrm{T} = m_0 c^2\left((1-\beta^2)^{-\frac{1}{2}} - 1\right)$$

is the kinetic energy of the particle.

β = ratio of velocity of β particle to the velocity of light.

K is a function of the velocity which increases slowly with increasing velocity. If we assume K is constant, and

integrate to find the thickness of matter R in which the kinetic energy is destroyed, we get

$$\int_0^R dx = \int_0^\beta -\frac{1}{K}\beta^2 dT$$

$$= \int_0^\beta -\frac{c^2 m_0}{K}\beta^2 d\{(1-\beta^2)^{-\frac{1}{2}}\},$$

$$R = \frac{c^2 m_0}{K}\left[(1-\beta^2)^{\frac{1}{2}} + (1-\beta^2)^{-\frac{1}{2}} - 2\right]$$

$$= \frac{c^2 m_0}{K} A,$$

where $\quad A = \left[(1-\beta^2)^{\frac{1}{2}} + (1-\beta^2)^{-\frac{1}{2}} - 2\right].$

In the following table in column I. is given the value of $H\rho$ in gauss cm. In column II. the value of β deduced from the relativity formula

$$\frac{m}{m_0} = (1-\beta^2)^{-\frac{1}{2}}$$

and $\quad H\rho = \frac{m}{e}c\beta, \qquad (c = \text{velocity of light}).$

$$\frac{e}{m_0} = 1{\cdot}772 \times 10^7 \text{ e.m. units.}$$

1.	II.	III.	IV.	V.	VI.
$H\rho$.	β.	$T/m_0 c^2$.	A.	R(obs.).	R/A.
1380	·632	·290	·0651	(·018)	(·30)
1930	·752	·516	·176	·064	·369
2535	·831	·799	·355	·124	·349
3170	·882	1·121	·584	·189	·325
3790	·9129	1·456	·863	·279	·323
4400	·9331	1·782	1·142	·360	·315
5026	·9476	2·131	1·45	·440	·304
6230	·9650	2·810	2·07	·580	·280
7490	·9753	3·531	2·75	·785	·285
8590	·9811	4·165	3·369	·925	·275
11370	·99		5·30	1·36	·26

The values of R(obs.) are expressed in gm. per sq. cm.

In column III. the value of $T/m_0 c^2$ is given. In column IV. the value of A. In column V. the value of R, the range observed from experiments, and in column VI., R(obs.)/A.

$\dfrac{\text{R(obs.)}}{\text{A}}$ ought to be equal to $c^2 m_0 / K$. With the exception of the first value, we see that $\dfrac{\text{R(obs.)}}{\text{A}}$ decreases slowly with increasing velocity, as should be expected from theory since K increases slowly with increasing velocity.

The fact that the aluminium absorption curve is approximately linear must result from a chance balancing of the opposing effects of scattering and diminution of velocity. If we had no scattering or straggling we should expect to have a curve similar in shape to a Bragg α-ray curve.

For a substance like paper, which contains only elements of low atomic weight, the effect of scattering is less important than for aluminium, so that a greater fraction of β rays will penetrate a given thickness of matter. This is seen from the fact that the absorption curve for filter-paper (fig. 6) is

Fig. 6.
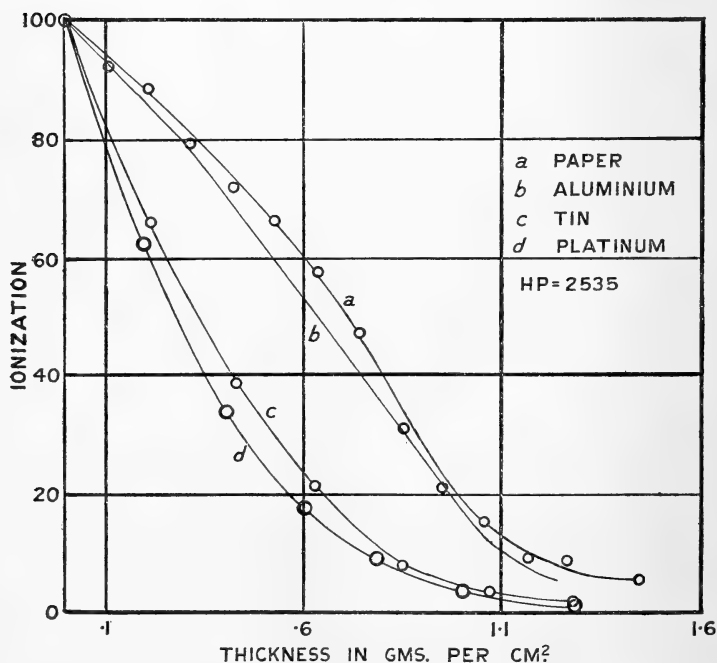
concave to the origin. For substances, like tin and platinum, of high atomic weight fewer β particles penetrate a given thickness, and the curves are convex towards the origin (fig. 6).

W. Wilson [*] has discussed the question of absorption of swift β rays by aluminium in two papers. The results given in his first communication agree approximately with those given in the present paper. He examined this question again in a second investigation, in which he believed that he obtained more homogeneous β rays. In this paper he finds that the absorption curve for fast rays in aluminium rises to a maximum for a small thickness of matter and then decreases in an approximately linear relation. His method of measuring the ionization due to the β rays was to subtract the reading of the electroscope with a thick screen from the reading with the screen in which the absorption of the β rays was under examination. Thus he assumes that the γ radiation produces the same quantity of secondary β radiation in a thick plate as in a thin plate. In general this is not the case. The conditions of his experiment are not sufficiently clear to form an idea of the magnitude of this correction; for it will depend on what material he placed in front of his ionization vessel (behind the aluminium screen). In my experiments, with celluloid in this position, the secondary β-ray effect was greater with a thick aluminium plate than with a thin one, as is shown in curve BB (fig. 2). If this were the case in Wilson's experiment, the rise of his absorption curve to a maximum receives a simple explanation. This is rendered the more probable since he mentions that the γ-ray effect was relatively strong, thus giving a relatively great importance to the secondary β rays from the absorbing screens. I have tried to obtain his results by narrowing the slits to produce greater purity of rays, but have been unsuccessful. In Wilson's experiment the air was not exhausted from the apparatus. To test the effect of this, readings were taken with air in the box B (fig. 1), but the only obvious effect was a diminution in intensity of the β radiation.

In conclusion I wish to thank Prof. Sir Ernest Rutherford for suggesting this research and for many valuable suggestions during its progress. I also wish to thank Dr. N. Bohr for his great interest and help in connexion with the theory of absorption of β particles.

The Physics Laboratory,
Victoria University of Manchester,
March 4, 1915.

[*] W. Wilson, Proc. Roy. Soc. A. lxxxii. p. 612 (1909); lxxxvii. p. 310 (1912).

LXXVII. *Photo-electric Constant and Atomic Heat.* *By* T. Carlton Sutton, *B.Sc., Government Research Scholar in the University of Melbourne* [*].

$\mathbf{T}$HE photo-electric constant, k, as used in this paper is defined (Jeans [†]) according to the relation

$$k\nu = \tfrac{1}{2}mv^2 + w_0,$$

where $\tfrac{1}{2}mv^2$ is the kinetic energy of an electron driven out of a metal by a radiant beam of wave-length ν, and w_0 (a constant for any particular metal) is the energy required to move the electron from within the atom to a point outside the sphere of action of the atom.

Hence, kv is the total energy required to expel an electron from the atom with velocity v.

The figures given in the accompanying table (column 6) show that the values of k do not vary greatly from that of one quantum, namely $6 \cdot 6 \times 10^{-27}$ erg ; though there are deviations (the values are invariably low) which have been said to depend in some way on the atomic volume [‡].

Some such idea as an indivisible unit or "quantum" of energy is suggested by the fact that the atomic heats of all elements have approximately the same value ; that is to say, it requires the same amount of heat-energy to change the temperature of any atom a given amount, irrespective of the nature of that atom.

Here, again, there are deviations from the mean value $6 \cdot 4$.

When the divergences of the atomic heats are compared with those of the photo-electric constants, a remarkable regularity is noticed. Thus, when the atomic heat is high, the photo-electric constant is low, and *vice versa,* except in the case of tin and of certain elements of low atomic weight (magnesium, aluminium, copper), which show an anomalously large change of atomic heat with temperature. In these exceptional cases, both values are low at ordinary temperatures, but as the temperature rises the atomic heat increases and the said regularities appear (see Table).

That this relation holds good is shown in the last column of the table, where the product has been taken of the atomic heat and the photo-electric constant, and has been found to give in almost every case a value close to $35 \cdot 5$.

	Atomic Weight.	Specific Heat.	Observer.	Atomic Heat.	Photo-electric Constant.	Observer.	Product. (A.H. × P.E.C. × 10²⁷.)
Cadmium	112·4	0·055	Voigt (1893).	6·18	$5·67 \times 10^{-27}$	Hughes.	*35·1*
Zinc	65·4	0·93	Various.	6·08	5·88	,,	*35·7*
Lead	207·1	0·031	Behn (1898).	6·41	5·50	,,	*35·2*
Calcium..........	40·1	0·180	Bunsen.	7·22	4·91	,,	*35·4*
Bismuth..........	208·0	0·030	Voigt (1893).	6·24	5·63	,,	*35·2*
Antimony	120·2	0·0508	Gaede (1902),	6·20	5·72	,,	*35·5*
Arsenic	75·0	0·083	Bettendorf & Wüllner.	6·23	5·7	,,	*35·5*
Sodium.	23·0	0·297	Bernini (1906),	6·83	5·2	R. & C.	*35·5*
Platinum	195·2	0·0316	Gaede (1902).	6·17	5·85	,,	*36·1*
Magnesium	24·3	at 20° C. 0·246 / at 225° C. 0·281	Voigt (1893). / Stucher (1905).	5·98 / 6·83	5·24	Hughes.	*31·3 at 20° C.* / *35·8 at 225° C.*
Aluminium	27·1	at 20° C. 0·219 / at 625° C. 0·308	Tilden (1903). / Boutschew.	5·93 / 8·35	4·3	R. & C.	*25·5 at 20° C.* / *35·9 at 625° C.*
Copper	63·57	at 20° C. 0·094 / at 900° C.0·126	Various. / Richards (1893).	5·98 / 8·01	3·8	,,	*28·6 at 20° C.* / *30·4 at 900° C.*
Tin..........	119·0	0·055	Various.	6·55	4·9	,,	*32·1*

The physical interpretation of this relation is difficult at present. It would seem, however, that

(1) Both phenomena are due to the "ultimate discontinuity" of energy as postulated in the quantum theory;

(2) When a limited number of quanta are absorbed by a molecule, the various properties of the molecule are not necessarily affected to the same extent—as some quanta may function in one way, some in another;

(3) For any particular metal, the proportion that affects the atomic heat is related to the proportion that affects the photo-electric constant; and if the nature of the metal is changed, this relation is one of inverse proportion.

The work of Nernst and Debye * shows that the atomic heat at constant volume is a more reliable physical constant than the atomic heat at constant pressure (the quantity usually measured). The atomic heats at constant volume all tend asymptotically to the same limiting high-temperature value, 5·95; whereas the atomic heats at constant pressure approach values which are different for different elements. The magnitude of the difference between the values of the two atomic heats is dependent on the amount of work required to compress the heated solid block to the volume it occupied when unheated; that is to lessen the amplitude of swing of the minute vibrating systems.

Consequently, the results given in this paper suggest that the divergences of the values of the photo-electric constant from the value of one quantum, $6·6 \times 10^{-27}$, are due to the work done in changing the amplitude of swing of the newly-charged atoms left within the metal.

My thanks are due to Mr. I. O. Masson for kindly correcting the proofs.

The University, Melbourne.

LXXVIII. *On a Tidal Problem.*
By Prof. H. LAMB *and* Miss L. SWAIN [*].

THE object of this note is to illustrate the theory of the
tides in a very simple case, viz., that of an equatorial
canal of finite length, the tide-generating body (say the
moon) being supposed to revolve uniformly in the plane of
the equator. Simple as the question is, the results are hardly
intelligible without detailed numerical or graphical inter-
pretation. Moreover, the problem is at present almost the
only one which can be used to exemplify a point of some
importance in tidal theory.

On Laplace's dynamical theory, as on the equilibrium
theory, there is necessarily exact agreement (or exact oppo-
sition) of phase between the tidal elevation and the forces
which generate it, in the case of an ocean covering the globe
or bounded by parallels of latitude, the depth being supposed
either uniform or a function of latitude only. The con-
spicuous and varied differences of phase which are observed
were accounted for in a general way by Newton [†], as due to
the inertia of the water combined with the irregular con-
figuration of the actual oceans. On the other hand, Airy, in
his 'Tides and Waves' (1845), attached great importance to
the action of friction, and appears to have regarded the
phase-differences in question as attributable mainly to this
cause. This view seems to have met with wide acceptance,

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favoured no doubt by the prominent part which was being assigned to tidal friction in various cosmical theories.

Qualitatively there is of course nothing to be said against Airy's explanation. The chief example considered by him, viz., that of an equatorial canal encircling the globe, is merely a particular case of the now familiar theory of forced oscillations with damping. If ϕ be a normal coordinate of a dynamical system we have, on the simplest assumption as to the nature of the dissipative forces, an equation of the type

$$\ddot{\phi} + k\dot{\phi} + \mu\phi = \Phi. \quad \ldots \quad \ldots \quad (1)$$

For the free oscillations

$$\phi = A e^{-t/\tau} \cos(\sigma t + \epsilon), \quad \ldots \quad \ldots \quad (2)$$

where $\quad\quad \tau = 2/k, \quad\quad \sigma = \sqrt{(\mu - \tfrac{1}{4}k^2)} \; ; \quad \ldots \quad (3)$

whilst if $\quad\quad\quad\quad \Phi = C \cos pt \quad \ldots \quad \ldots \quad (4)$

we have the forced oscillation

$$\phi = \frac{C}{R} \cos(pt - \beta) \quad \ldots \quad \ldots \quad (5)$$

provided

$$R \cos\beta = \mu - p^2, \quad\quad R \sin\beta = kp. \quad \ldots \quad (6)$$

There is here a retardation of phase given by

$$\tan\beta = \frac{kp}{\mu - p^2} = \frac{2}{p\tau(\mu/p^2 - 1)}. \quad \ldots \quad (7)$$

In the tidal problem $p = 2n$, where n is the moon's angular velocity relative to the rotating earth.

The question remains, however, whether the frictional forces which are operative are sufficient to account for the observed differences. It was pointed out by Helmholtz [*] in 1888 that the influence of viscosity on large-scale motions of the atmosphere must be absolutely insignificant, and it was easy to infer that the same conclusion must hold *à fortiori* as regards tidal oscillations of water [†], where the kinematic viscosity is much less. This point was afterwards fully developed by Hough [‡], who showed in particular that with even so moderate a depth as 200 metres the modulus of decay (τ) of free tidal motions of semidiurnal type would be at least three years. It may indeed be urged that in places where the tides are greatly exaggerated, as in narrow channels and estuaries, there may be turbulent motions with a local dissipation of energy far exceeding what takes place

[*] *Berl. Sitzb.*, May 31, 1888; *Wiss. Abh.* Bd. iii. p. 292.
[†] 'Hydrodynamics,' 2nd ed. (1895) p. 543.
[‡] Proc. Lond. Math. Soc. vol. xxviii. p. 287 (1896).

in the smooth regular motions postulated in the calculations referred to, and it is possible that such tidal retardation of the earth's rotation as is taking place under present conditions may be mainly due to this cause. It may fairly be assumed, however, as a matter of physical intuition, apart from calculation, that the damping of free oscillations of the ocean of semidiurnal type would hardly be sensible until after the lapse of a considerable number of periods.

If this be granted, it follows from (7) that the phase-difference produced by friction in an endless equatorial canal would be insignificant. With such depths as occur in the ocean μ is considerably less than p^2, and $\tan \beta$ is therefore comparable in absolute value with T/τ, where $T(=2\pi/p)$ is the period of the forced oscillation. The modulus of decay being assumed to be large compared with 12 hours, β must differ very little from $180°$. A phase-difference of $90°$, such as is postulated in some numerical illustrations of the theory of tidal friction, could only arise exceptionally, by " resonance," in the case of finite areas of water having a free period very closely in accordance with the forced period.

It seems clear that the influence of friction on ordinary tidal phenomena is unimportant. It was pointed out by Hough in the paper referred to that phase-differences must arise in another way, from the causes indicated by Newton, in limited canals or oceans [*]. He remarks also that an example in illustration of this is furnished by the problem of the finite canal which had been treated, but not fully examined, by Airy himself.

Moreover, it should not be overlooked that a mere equilibrium theory, when " corrected " on the principles explained by Thomson and Tait, would also give differences of phase [†]. Consider for example the case of a canal a few degrees in length lying along the equator. When the moon (or antimoon) is in the zenith the differential changes of level are everywhere slight, the disturbing force being nearly vertical and uniform. When the moon is on the horizon, the changes are again slight, since moon and antimoon now nearly counteract one another as regards the horizontal force. Hence *at the ends* of the canal there will be high or low water for some intermediate position; the theory shows in fact that the corresponding hour-angle is $45°$. At the *centre* the range is comparatively small, and high water coincides with the moon's (or antimoon's) transit.

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[*] In seas whose breadth as well as length has to be taken into account the question is further complicated by the " gyrostatic " effect of the earth's rotation.

[†] Thomson and Tait, Art. 810; 'Hydrodynamics,' 3rd. ed. p. 341.

The calculations which follow will serve to illustrate the foregoing remarks. The formulæ were worked out originally in response to an inquiry addressed to one of the writers from abroad, and in ignorance, or more probably in forgetfulness of the fact that the matter had already been treated to some extent by Airy, and referred to by Hough.

We consider the case of an equatorial canal of uniform depth h, the moon being supposed to revolve in the plane of the equator. If θ denote longitude measured eastwards from a fixed meridian, and nt the hour-angle of the moon west of this meridian, the dynamical equation is of the form

$$\frac{\partial^2 \xi}{\partial t^2} = \frac{c^2}{a^2} \frac{\partial^2 \xi}{\partial \theta^2} - f \sin 2(nt + \theta), \quad . \quad . \quad . \quad (8)$$

where a is the earth's radius, $c^2 = gh$, and ξ denotes horizontal displacement eastwards[*].

For an equilibrium theory we neglect the term $\partial^2 \xi / \partial t^2$. If the origin of θ be taken at the centre of the canal, we find

$$\xi = \frac{1}{4} \frac{f a^2}{c^2} \left\{ \sin 2nt \cos 2\alpha + \frac{\theta}{\alpha} \cos 2nt \sin 2\alpha - \sin 2(nt + \theta) \right\};$$
$$. \quad . \quad . \quad (9)$$

for this expression satisfies the differential equation, and makes $\xi = 0$ at the ends $(\theta = \pm \alpha)$. For the surface-elevation we have

$$\eta = -\frac{h}{a} \frac{\partial \xi}{\partial \theta} = \frac{1}{2} H \left\{ \cos 2(nt + \theta) - \frac{\sin 2\alpha}{2\alpha} \cos 2nt \right\},$$
$$. \quad . \quad . \quad (10)$$

where $H = f a / g$. This quantity H measures, on the equilibrium theory, the maximum range of the tide in the case of an ocean covering the whole earth [†].

At the centre $(\theta = 0)$ we have

$$\eta = \frac{1}{2} H \cos 2nt \left(1 - \frac{\sin 2\alpha}{2\alpha} \right). \quad . \quad . \quad (11)$$

If α be small, the range here is very small, but there is not a *node* in the strict sense of the term. The times of high water coincide with the transits of the moon and antimoon.

At the ends $(\theta = \pm \alpha)$, we find

$$\eta = \frac{1}{2} H \left\{ \left(1 - \frac{\sin 4\alpha}{4\alpha} \right) \cos 2(nt \pm \alpha) \mp \frac{1 - \cos 4\alpha}{4\alpha} \sin 2(nt \pm \alpha) \right\}$$

$$= \frac{1}{2} H \cdot R_0 \cos 2(nt \pm \alpha \mp \phi_0), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

if

$$R_0 \cos 2\phi_0 = 1 - \frac{\sin 4\alpha}{4\alpha}, \quad R_0 \sin 2\phi_0 = -\frac{1 - \cos 4\alpha}{4\alpha}. \quad . \quad (13)$$

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[*] 'Hydrodynamics,' Art. 180.
[†] 'Hydrodynamics,' Art. 179.

Here R_0 is the ratio of the range of the tide to the quantity H, and ϕ_0 denotes the hour-angle of the moon W. of the meridian when there is high water at the *eastern* end of the canal; it is also the hour-angle E. of the meridian when there is high water at the *western* end [*]. When α is small we have

$$R_0 = 2\alpha, \quad \phi_0 = -\frac{1}{4}\pi + \frac{2}{3}\alpha, \quad . \quad . \quad . \quad (14)$$

approximately.

The values of R_0 and ϕ_0 for a series of values of α ranging from 0 to $\frac{1}{4}\pi$ are given in the table at the end of this paper, on the assumption that $h = 10820$ feet.

When the inertia of the water is taken into account, we have

$$\xi = \frac{1}{4}\frac{fa^2}{(m^2-1)c^2}\left[\sin 2(nt+\theta) - \frac{1}{\sin 4m\alpha}\left\{\sin 2(nt+\alpha)\sin 2m(\theta+\alpha)\right.\right.$$
$$\left.\left. - \sin 2(nt-\alpha)\sin 2m(\theta-\alpha)\right\}\right], \quad . \quad (15)$$

where $m = na/c$. For this satisfies (8), and vanishes for $\theta = \pm\alpha$ [†]. Hence

$$\eta = -\frac{h}{a}\frac{\partial\xi}{\partial\theta}$$

$$= -\frac{1}{2}\frac{H}{m^2-1}\left[\cos 2(nt+\theta) - \frac{m}{\sin 4m\alpha}\left\{\sin 2(nt+\alpha)\cos 2m(\theta+\alpha)\right.\right.$$
$$\left.\left. - \sin 2(nt-\alpha)\cos 2m(\theta-\alpha)\right\}\right]. \quad . \quad (16)$$

An equivalent form is

$$\eta = -\frac{1}{2}\frac{H}{m^2-1}\left[\cos 2(nt+\theta) - \frac{m}{\sin 4m\alpha}\left\{\cos 2(nt+m\theta)\sin 2(m+1)\alpha\right.\right.$$
$$\left.\left. - \cos 2(nt-m\theta)\sin 2(m-1)\alpha\right\}\right]. \quad (17)$$

If we imagine m to tend to the limit 0 we obtain the formula (12) of the equilibrium theory. It may be noticed that the expressions do not become infinite for $m\to 1$, as in the case of a canal encircling the globe. In all cases, however, which are at all comparable with oceanic conditions, m is considerably greater than unity.

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[*] The *phase*-difference is $2\phi_0$. This angle, reckoned in degrees from 0 to 360°, is called by Darwin and Baird the "lag" of the tide, Proc. Roy. Soc. vol. xxxix. p. 135 (1885).

[†] *Cf.* Airy, 'Tides and Waves,' Art. 301.

At the middle point of the canal we have

$$\eta = -\frac{1}{2}\frac{H}{m^2-1}\cos 2nt\left(1-\frac{m\sin 2\alpha}{\sin 2m\alpha}\right). \quad . \quad (18)$$

As in the equilibrium theory, the range is very small if α be small, but there is not a true node.

At the ends $\theta = \pm\alpha$ we find

$$\eta = \frac{1}{2}\frac{H}{m^2-1}\left\{\left(\frac{m\sin 4\alpha}{\sin 4m\alpha}-1\right)\cos 2(nt\pm\alpha)\right.$$

$$\left.\pm\frac{m(\cos 4m\alpha-\cos 4\alpha)}{\sin 4m\alpha}\sin 2(nt\pm\alpha)\right\}. \quad . \quad (19)$$

$$= \frac{1}{2}HR_1\cos 2(nt\pm\alpha\mp\phi_1), \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

if
$$R_1\cos 2\phi_1 = \frac{m\sin 4\alpha - \sin 4m\alpha}{(m^2-1)\sin 4m\alpha}, \quad \left.\begin{array}{c} \\ \\ \end{array}\right\} \quad . \quad . \quad (21)$$
$$R_1\sin 2\phi_1 = \frac{m(\cos 4m\alpha - \cos 4\alpha)}{(m^2-1)\sin 4m\alpha}.$$

The significance of the quantities R_1, ϕ_1 is the same as in the equilibrium formula (13) *. When α is small we have

$$R_1 = 2\alpha, \quad \phi_1 = -\frac{1}{4}\pi + \frac{2}{3}\alpha, \quad . \quad . \quad . \quad (22)$$

approximately, as before.

The values of R_1 become infinite for $\sin 4m\alpha = 0$. This determines the critical lengths of the canal for which there is a free period equal to π/n, or half a lunar day. The limiting value of ϕ_1 in such a case is given by

$$\tan 2\phi_1 = \frac{m(\cos 4m\alpha - \cos 4\alpha)}{m\sin 4\alpha - \sin 4m\alpha} = -\cot 2\alpha, \text{ or } \tan 2\alpha, \quad . \quad (23)$$

according as $4m\alpha$ is an odd or even multiple of π.

For purposes of numerical illustration we have taken $m = 2\cdot5$. If $\pi/n = 12$ lunar hours, this implies a depth of 10820 feet, which is of the same order of magnitude as the mean depth of the ocean. The corresponding wave-velocity c is 360 sea miles per lunar hour. The first critical length is 2160 miles $\left(\alpha = \frac{1}{10}\pi\right)$, and the second is 4320 miles.

The table gives results for a series of lengths varying from 0 to 5400 miles. The unit in terms of which the range is expressed is the quantity H, whose value for the lunar tide is about 1·80 ft. The hour-angles ϕ_0 and ϕ_1 have been adjusted so as to lie always between $\pm 90°$, and the positive sign denotes position W. of the meridian in the case of the eastern end of the canal, and E. of the meridian in the case of the western end.

The diagrams show successive forms of the wave-profile on the dynamical theory in the case of $2\alpha = 18°$, corresponding to a length of 1080 miles. In fig. 1 the curve a corresponds

Fig. 1.
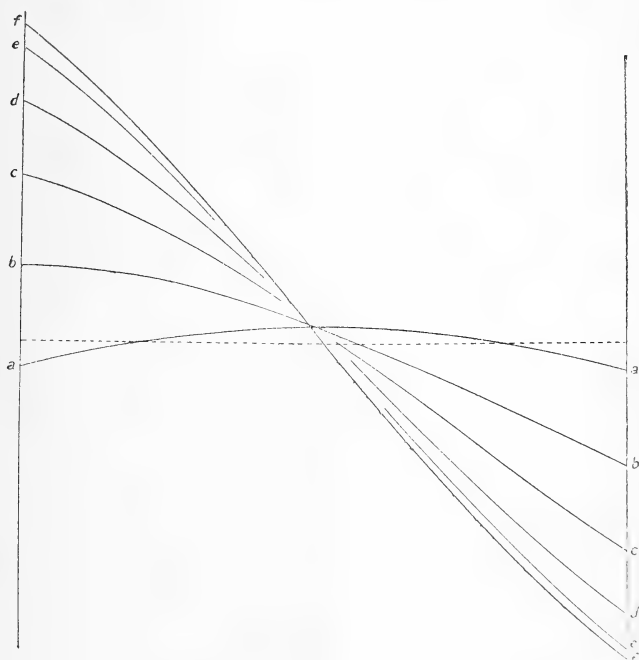
to the instant when the moon (or antimoon) is over the centre of the canal, and the following curves b, c, d, e, f represent the profile at intervals of one-twentieth of a period, or 36 minutes. Only one quarter of a complete cycle is shown ; the remaining curves might be obtained by reflexions with respect to vertical and horizontal axes through the centre.

In fig. 2 the neighbourhood of the centre is represented on a larger scale, with a view to showing how the phase-difference rapidly varies from 0 at the centre towards the value 77° which obtains at the ends.

Fig. 2.
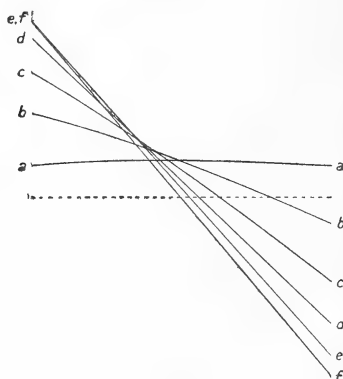
2α (degrees).	2aα (miles).	EQUILIBRIUM THEORY.			DYNAMICAL THEORY.		
		Range at centre.	Range at ends.	φ₀ (degrees).	Range at centre.	Range at ends.	φ₁ (degrees).
0	0	0	0	*−45*	0	0	*−45*
4·5	270	·001	·079	*−43·5*	·001	·080	*−43·5*
9	540	·004	·157	*−42*	·004	·165	*−41·9*
13·5	810	·009	·234	*−40·5*	·010	·266	*−40·3*
18	1080	·016	·311	*−39*	·018	·396	*−38·5*
22·5	1350	·025	·386	*−37·5*	·029	·588	*−36·4*
27	1620	·037	·460	*−36*	·044	·941	*−33·9*
31·5	1890	·050	·531	*−34·5*	·063	1·945	*−30·9*
36	2160	·065	·601	*−33*	·089	∞	{ *−27* / *+63* }
40·5	2430	·081	·668	*−31·6*	·125	1·956	*+68·2*
45	2700	·100	·733	*−30·1*	·174	·987	*+75·7*
49·5	2970	·120	·795	*−28·7*	·245	·711	*+85·3*
54	3240	·142	·853	*−27·2*	·354	·660	*−83·5*
58·5	3510	·165	·908	*−25·8*	·540	·780	*−73*
63	3780	·190	·959	*−24·4*	·918	1·141	*−65·1*
67·5	4050	·216	1·007	*−23*	2·067	2·294	*−58·9*
72	4320	·243	1·051	*−21·6*	∞	∞	{ *−54* / *+36* }
76·5	4590	·272	1·091	*−20·2*	2·564	2·302	*+40·3*
81	4860	·301	1·127	*−18·9*	1·459	1·112	*+44·5*
85·5	5130	·332	1·158	*−17·5*	1·035	·715	*+49·4*
90	5400	·363	1·185	*−16·2*	·864	·513	*+55·9*

LXXIX. *On Topic Parameters and Morphotropic Rela-
tionships. By* William Barlow, *F.R.S., and* William
Jackson Pope, *F.R.S.*[*]

TOPIC parameters were introduced by Becke (*Anz. d.
Kais. Akad. d. Wiss., Wien*, xxx. 1893, 204) for
defining, as between crystallographically related substances,
the lineal dimensions of the corresponding crystal structures ;
in a substance crystallizing in one of the rectangular systems,
the topic parameters, χ, ψ and ω, are calculated as

$$\chi = \sqrt[3]{(a^2 V/c)} \; ; \;\; \psi = \chi/a \; ; \;\; \omega = \psi c,$$

a, *b*, and *c* being the crystallographic axial ratios and V the
molecular volume of the substance.

The topic parameters of a set of isomorphously related
substances define the actual changes in dimensions of the
point system which attend the passage from one crystalline
substance to others isomorphous with it. During a number
of years past, however, it has been customary to calculate
and record the topic parameters of series of substances the
members of which exhibit any chemical or morphotropic
relationship ; so far as we are aware, no fact or conclusion
of importance has resulted from the application of the topic
parameters to cases of morphotropic relationship as distinct
from those of isomorphism.

That topic parameters, as hitherto applied to the quanti-
tative description of morphotropy, are without physical
significance is well illustrated by a consideration of the
particular case generally chosen in explanation of the subject.
The instance in question refers to the morphotropic relation-
ship between ammonium iodide and its tetramethyl, tetra-
ethyl, and tetrapropyl derivatives, and derives authority
from the important position assigned to it in a number of
our most valued text-books (Groth, ' Einleitung in die
chemische Krystallographie,' 1904. p. 32; Groth, ' Chemische
Krystallographie,' i. 1906, p. 171 ; Nernst, ' Theoretische
Chemie,' Siebente Aufl., 1913, p. 373 ; Roscoe and Schor-
lemmer, ' Treatise on Chemistry,' vol. ii. 1907, p. 220; Barker,
in same, vol. ii. 1913, p. 220); more recently Groth has again
referred to the importance of this example (*Zeits. f. Kryst.*
liv. 1914, p. 68). The data were collected by Slavik (*Zeits.
f. Kryst.* xxxvi. 1902, p. 268), and his interpretation of the
meaning of the topic parameters was confirmed and amplified
by Wagner (*Zeits. f. Kryst.* xliii. 1907, p. 148). Slavik

* Communicated by the Authors.

determined the following axial ratios, &c., in connexion with
the subject under discussion.

	Crystal System.	V.	Axial Ratios.
NH_4I	Cubic.	57·51	
$N(CH_3)_4I$ ...	Tetragonal.	108·70	$a : c = 1 : 0·7223.$
$N(C_2H_5)_4I$ ...	Tetragonal.	162·91	$a : c = 1 : 0·5544.$
$N(C_3H_7)_4I$ ...	Rhombic.	235·95	$a : b : c = 0·7761 : 1 : 0·6283.$

The following table, giving the topic parameters calculated
from the above data and stating the changes which they expe-
rience throughout the series, is taken from Nernst (*loc. cit.*).

	$NH_4I.$	Δ	$NMe_4I.$	Δ	$NEt_4I.$	Δ	$NPr_4I.$
V	57·51	51·19	108·70	54·21	162·91	73·04	235·95
χ	3·860	1·459	5·319	1·329	6·648	−0·555	6·093
ψ	3·860	1·459	5·319	1·329	6·648	1·103	7·851
ω	3·860	−0·018	3·842	−0·156	3·686	1·247	4·933

The conclusion drawn by Slavik from this table, and
repeated in the text-books mentioned, is that on passing from
the cubic ammonium iodide to the tetragonal tetramethyl-
ammonium iodide one dimension of the crystal structure,
that of ω, remains sensibly unchanged, and that the main
increase in dimensions of the crystal structure occurs in the
two directions of χ and ψ. Similarly, in passing from the
tetramethyl- to the tetraethyl-ammonium iodide, the
dimension ω again changes but little and, as before, the chief
increase in dimensions of the structure occurs in χ and ψ.

This interpretation, which has been so widely adopted as
illustrating the value of the topic parameters in elucidating
morphotropy, appears to us entirely erroneous for the
following reasons :—The method adopted for the description
of the tetragonal tetramethylammonium iodide gives to the
chief forms present the indices {100} and {111} ; the
descriptions given by Slavik and by Wagner show that
the salt crystallizes in combinations of {100} and {111},
resembling rhombic dodecahedra of the cubic system in that
the angle 110 : 111 = 44° 23′ 30″. It is clear, therefore, that
in accordance with Fedorow's practice of assigning the most
simple set of indices to the forms exhibited, the indices
{100} and {111} should be changed to {110} and {101}
respectively ; when this change is made the axial ratio
becomes

$$a : c = 1 : \text{cotan. } 44° 23′ 30″ = 1 : 1·0214.$$

This mode of interpreting the goniometrical data, which is a more rational one than that applied by Slavik and Wagner, shows that the salt is markedly pseudo-cubic. So that in passing from the cubic ammonium iodide to the pseudo-cubic tetragonal tetramethylammonium iodide, the three equal topic parameters of the first, $\sqrt[3]{57 \cdot 5} = 3 \cdot 9$, change almost equally to approximately $\sqrt[3]{108 \cdot 7} = 4 \cdot 8$. This necessary alteration in the table of topic parameters reproduced above entirely destroys the sequence as between ammonium iodide, tetramethylammonium iodide, and tetraethylammonium iodide; the table in question is thus valueless as an illustration of the use of these parameters in exhibiting morphotropic relationships.

A broad view of the morphotropic relationships holding between the ammonium halides and their tetraalkyl derivatives is obtained by considering the axial ratios and crystal systems presented by a number of related compounds which exhibit high crystalline symmetry.

KI	Cubic.	
NH_4I	,,	
$(CH_3)_4NCl$	Tetragonal.	$a : c = 1 : 0 \cdot 7107$.
$(CH_3)_4NBr$	,,	$a : c = 1 : 0 \cdot 7131$.
$(CH_3)_4NI$	,,	$a : c = 1 : 0 \cdot 7223$.
$(CH_3)_4SbI$	Hexagonal.	$a : c = 1 : 1 \cdot 422$.
$(C_2H_5)_4NI$	Tetragonal.	$a : c = 1 : 0 \cdot 5544$.
$(C_2H_5)_4PI$	Trigonal.	$a : c = 1 : 1 \cdot 4719$.
$(C_2H_5)_4NBr$	,,	$a : c = 1 : 1 \cdot 4656$.
$(CH_3)H_3NI$	Tetragonal.	$a : c = 1 : 1 \cdot 467$.
$(C_2H_5)_3HNCl$	Hexagonal.	$a : c = 1 : 0 \cdot 8451$.
$(C_2H_5)_3HNBr$ ...	,,	$a : c = 1 : 0 \cdot 8746$.
$(C_2H_5)_3(CH_3)NI$ ..	Tetragonal.	$a : c = 1 : 0 \cdot 5536$.

The table shows that on replacing the metallic atom in potassium iodide by the ammonium radicle, NH_4, the system retains its cubic symmetry; on replacing each of the four hydrogen atoms in the ammonium halide by methyl, pseudo-cubic symmetry results in the manner described in detail above. The general applicability of the principle thus stated is demonstrated by the similar axial ratios exhibited by tetramethylammonium chloride, bromide, and iodide; similarly, on replacing one of the hydrogen atoms in the ammonium iodide molecule by a methyl group, so as to

produce the tetragonal methylammonium iodide, the axial ratio, $c/a = 1\cdot467$, indicates that pseudo-cubic symmetry again results, this value of c/a being comparable to that of $2c/a$ in tetramethylammonium iodide.

On substituting an atom of antimony for one of nitrogen in tetramethylammonium iodide, so as to obtain tetramethyl-stibonium iodide, $(CH_3)_4SbI$, the tetragonal symmetry changes to hexagonal with the axial ratio, $a : c = 1 : 1\cdot422$. An hexagonal system showing an axial ratio of this order of magnitude is closely related to the cubic system for the following reasons :—If a cube diagonal, which is a trigonal axis of symmetry, is taken as the vertical axis-c of a system of crystallographic coordinates of a trigonal or hexagonal kind, one of the two obvious horizontal translations is twice the distance between a cube corner and the centre of an opposite cube face ; taking the cube edge as of unit length, the diagonal is $\sqrt{3}$ and the distance from the cube corner to the centre of an opposing face is $\sqrt{(3/2)}$. The axial ratio corresponding to this mode of referring a cube to a set of trigonal coordinates is, therefore, $a : c = \sqrt{(3/2)} : \sqrt{3} = 1 : 1\cdot4142$. The trigonal or hexagonal tetramethylstibonium iodide, tetraethyl-phosphonium iodide and -ammonium bromide obviously approximate closely to these dimensions.

The hexagonal axial ratio alternative to the value, $a : c = 1 : 1\cdot4142$, is $a : c = 1 : 1\cdot6330$ (Trans. Chem. Soc. xci. 1907, p. 1157) and the values recorded for triethyl-ammonium chloride and bromide are rather more than one-half of this, namely, $a : c = 1 : 0\cdot8165$; these two substances may therefore also be regarded as morphologically related in a simple manner to the cubic ammonium halides.

The axial ratio, $a : c = 1 : 0\cdot5544$, of the tetragonal tetraethyl-ammonium iodide is also, though somewhat less distinctly, that of a pseudo-cubic substance, because on multiplying unit length along the axis-c by two, it assumes the pseudo-cubic form, $a : c = 1 : 1\cdot1088$. Ample justification can be given for altering this axial ratio in this manner ; this substance is of the same type as the hexagonal tetramethylstibonium iodide and tetraethylammonium bromide which have already been shown to be morphologically closely related to the cubic system.

A comparison of the measured angles on tetraethyl-ammonium iodide with principal measured angles on the

other two compounds mentioned shows that a very complete correspondence exists.

$(C_2H_5)_4NBr.$	$(C_2H_5)_4NI.$	$(C_2H_5)_4PI.$	$(C_2H_5)_3(CH_3)NI.$
$31\bar{1}:13\bar{1}=52° 52'$	$111:110=51° 54'$	$31\bar{1}:13\bar{1}=52° 55'$	$111:1\bar{1}1=51° 56'$
	$111:\bar{1}\bar{1}1$ 76 12	$13\bar{1}:100$ 76 5	$111:\bar{1}\bar{1}1$ 76 7
$31\bar{1}:111$ 62 54	$111:100$ 64 8	$31\bar{1}:111$ 63 2	

It thus appears that the basal plane (111) on the trigonal compounds corresponds to the pinacoid (001) on the tetragonal one, the rhombohedron (100) and the pyramid $(31\bar{1})$ on the former also corresponds to the pyramid $(\bar{1}\bar{1}1)$ and the prism (110) on the latter. The tetragonal tetraethyl-ammonium iodide is therefore morphotropically closely related with the two trigonal substances, the dimensions of which have been shown to be pseudo-cubic.

The values for the tetragonal methyltriethylammonium iodide, with $a : c = 1 : 0·5536$, are included in the above table because, for the reasons just quoted, this substance must also be referred to the cubic system.

Without at present entering into detail as to the manner in which the mode of interpreting morphotrophic relation-ships which we have previously developed (Trans. Chem. Soc. lxxxix. 1906, p. 1675 ; xci. 1907, p. 1150 ; xciii. 1908, p. 1528 ; xcvii. 1910, p. 2308) is applicable to the present case, we may regard the following conclusion as definitely established. The method of representing the morphotropic relationship which exists between ammonium, tetramethyl-ammonium, tetraethylammonium, and tetrapropylammonium iodide advocated by Slavik and Wagner, and generally adopted in the text-book literature, has been proved to be incorrect and should be abandoned.

The fact that so many of the alkyl derivatives of the ammonium halides affect types of crystalline symmetry and axial ratios closely related to the cubic system is important ; it seems to be generically connected with the fact that the ammonia in aluminium ammonium alum can be replaced by hydroxylamine, methylamine, ethylamine, and trimethylamine, with retention of the original cubic symmetry.

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LXXX. *Construction of Cubic Crystals with Theoretical Atoms. By* ALBERT C. CREHORE, *Ph.D.*[*] (*From the Department of Physiology of Columbia University.*)

[Plate XI.]

IN a former paper upon this subject [†] there was developed a general expression for the instantaneous mechanical force which one electron revolving uniformly in a circular orbit exerts upon a second electron revolving in a different circular orbit. This is based upon the well-known equations for the mechanical force that one moving electrical charge exerts upon another ; but the velocity of transmission is taken as infinite to simplify matters, and reasons were given why it seems probable that the results obtained with these simpler initial equations would not be different if the more complicated general expressions were employed. The mechanical force between two rings of electrons is shown to be independent of the relative phase angles, and any retardation of the transmission velocity would be likely to affect only these phase angles, and not change the mechanical force.

In that paper the integral of the general equation was obtained in one special case only, namely, when the axes of revolution of the two electrons are parallel to each other and the angular velocities of orbital revolution are identical [‡]. The work of integrating for average velocities has now been completed in the most general case, when the two axes of revolution make any angle α with each other, and the frequencies of revolution are either incommensurable or equal to each other.

The General Equation.

Using the same notation as in the paper referred to, the total instantaneous mechanical force is expressed as the sum of four vector components. The first or electrostatic component is

$$F_1 = -\frac{ee'}{KR^3}R. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Here e and e' denote the two charges, each having the same sign, K the specific inductive capacity of the medium, and R the scalar instantaneous distance between the two charges.

[*] Communicated by the Author.
[†] A. C. Crehore, Phil. Mag. July 1913, p. 25.
[‡] *Loc. cit.* Equations (42) and (44). Note an omission in the co-efficients B, corrected in a note, page 325, Phil. Mag. Feb. 1915.

R is the vector from the charge e to e' varying with the time, and F_1 is the first component force which the second charge e' exerts upon e. Using the abbreviations

$$S = \sin(\omega t + \theta); \quad S' = \sin(\omega' t + \theta'); \quad C = \cos(\omega t + \theta);$$
$$C' = \cos(\omega' t + \theta'), \quad . \quad . \quad (2)$$

where ω and ω' are the angular velocities of the charges and θ and θ' their phase angles respectively, referred to fixed rectangular axes, it follows that

$$\mathbf{R} = (x - aS)i + (y - aC + a'C')j + zk + a'S'i', \quad . \quad (3)$$

where i, j, and k, i', j', and k' form two systems of rectangular axes, referred respectively to the centres of the orbits of e and e'. k and k' take the directions of the axes of revolution of the electrons, each being clockwise when observed from the positive side or pole. j and j' each take the direction of the line of intersection of the planes of the orbits, the positive direction along each being defined by the vector $k \times k'$. i and i' lie in the planes of the orbits respectively in such directions as to make the two systems of axes each have the conventional cyclic order i, j, k and i', j', k', in the counter-clockwise rotation when viewed from the positive side of each.

Hence
$$R^2 = s^2(1 + u), \quad . \quad . \quad . \quad . \quad . \quad (4)$$
where s is a constant,

$$s^2 = x^2 + y^2 + z^2 + a^2 + a'^2, \quad . \quad . \quad . \quad (5)$$

x, y, and z being the coordinates of the centre of the orbit of the second charge, a and a' the radii of the two orbits respectively, and u a function of the time such that

$$u = \frac{2}{s^2}\Big(-axS - ayC + a'zS' \sin \alpha + a'yC' + a'xS' \cos \alpha$$
$$- aa'SS' \cos \alpha - aa'CC' \Big). \quad . \quad . \quad (6)$$

If the force in (1) is resolved into three rectangular components along the i, j, and k axes, which may be done by taking the direct or dot products with i, j, and k in turn, we obtain, observing that $i'.i = \cos \alpha$, and $i'.k = \sin \alpha$,

$$\underset{x}{F_1} = -\frac{ee'}{KR^3}\Big(x - aS + a'S' \cos \alpha \Big)i, \quad . \quad . \quad (7)$$

$$\underset{y}{F_1} = -\frac{ee'}{KR^3}\Big(y - aC + a'C' \Big)j, \quad . \quad . \quad . \quad (8)$$

$$\underset{z}{F_1} = -\frac{ee'}{KR^3}\Big(z + a'S' \sin \alpha \Big)k. \quad . \quad . \quad . \quad (9)$$

Expressing all distances in some convenient small unit a_*, such as the radius of the orbit in the single electron atom, instead of in centimetres, and letting m and n represent the radii of the orbits and x_*, y_*, and z_* the coordinates in these units, we have

$$x = a_* x_*; \quad y = a_* y_*; \quad z = a_* z_*; \quad a = m a_*; \quad a' = n a_*. \quad (10)$$

The value of s in (5) becomes

$$s = a_*(x_*^2 + y_*^2 + z_*^2 + m^2 + n^2)^{\frac{1}{2}},$$

or, denoting the radical by Δ^{-1}, we have

$$s = a_* \Delta^{-1}, \quad \ldots \ldots \quad (11)$$

and from (4)

$$\mathrm{R}^{-3} = a_*^{-3} \Delta^3 (1+u)^{-\frac{3}{2}}. \quad \ldots \ldots \quad (12)$$

Hence, substituting in (7), (8), and (9),

$$\mathrm{F_1}_x = -\frac{ee'}{\mathrm{K} a_*^2} \Delta^3 (x_* - m\mathrm{S} + n\mathrm{S}' \cos\alpha)(1+u)^{-\frac{3}{2}} i, \quad (13)$$

$$\mathrm{F_1}_y = -\frac{ee'}{\mathrm{K} a_*^2} \Delta^3 (y_* - m\mathrm{C} + n\mathrm{C}')(1+u)^{-\frac{3}{2}} j, \quad \ldots \quad (14)$$

$$\mathrm{F_1}_z = -\frac{ee'}{\mathrm{K} a_*^2} \Delta^3 (z_* + n\mathrm{S}' \sin\alpha)(1+u)^{-\frac{3}{2}} k. \quad \ldots \quad (15)$$

This completes that part of the mechanical force which arises from the first or electrostatic component. It remains to consider the magnetic effect, which is derived from the three component forces given by equations (2), (3), and (4) of the former paper [*].

It has been previously shown [†] that the last two of these terms when integrated contribute nothing to the translational force of the one charge on the other, so that the total force will be obtained by considering, in addition to the preceding, the force

$$\mathrm{F_2} = +\frac{\mu e e'}{\mathrm{R}^3} (\mathbf{q} \cdot \mathbf{q'}) \mathbf{R}. \quad \ldots \ldots \quad (16)$$

Here the new quantities are μ, the magnetic permeability of the medium, and $\mathbf{q}$ and $\mathbf{q'}$, the vector velocities of the charges respectively. It was shown in the former paper that

$$\mathbf{q} \cdot \mathbf{q'} = aa' \, \omega\omega' \, (\mathrm{CC}' \cos\alpha + \mathrm{SS}'), \quad \ldots \quad (17)$$

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* *Loc. cit.* p. 58.
† *Loc. cit.* p. 63.

and putting $\mu = \dfrac{1}{Kc^2}$, where c is the velocity of light, we find

$$F_2 = + \frac{ee'\, aa'\, \omega\omega'}{Kc^2R^3}(CC' \cos \alpha + SS')\mathbf{R}. \quad . \quad . \quad (18)$$

Denoting the ratio of the velocities of the charges to that of light by β and β' respectively, resolving the force along the three rectangular axes as before, and substituting the value of R^3 as a function of the time, we find

$$\underset{x}{F_2} = + \frac{ee'}{Ka_*^2}\, \beta\beta'\Delta^3(CC' \cos a + SS')(x_* - mS + nS' \cos \alpha)(1 + u)^{-\frac{3}{2}}i, \quad (19)$$

$$\underset{y}{F_2} = + \frac{ee'}{Ka_*^2}\, \beta\beta'\Delta^3(CC' \cos a + SS')(y_* - mC + nC')(1 + u)^{-\frac{3}{2}}j, \quad . \quad (20)$$

$$\underset{z}{F_2} = + \frac{ee'}{Ka_*^2}\, \beta\beta'\Delta^3(CC' \cos \alpha + SS')(z_* + nS' \sin \alpha)(1 + u)^{-\frac{3}{2}}k. \quad . \quad (21)$$

The two sets (13)–(15) and (19)–(21) are the complete general equations for the instantaneous values of the electrostatic and magnetic components of the mechanical force exerted upon the charge e by the charge e', omitting the third and fourth components as above mentioned, which when averaged over a long period of time give zero. The only quantities in these equations dependent upon the time are the simple periodic functions S, S', C, and C', u being a polynomial of seven terms each containing some of these quantities. The expansion of $(1+u)^{-\frac{3}{2}}$ into infinite series to five terms is

$$1 - 1.5u + 1.875u^2 - 2.1875u^3 + 2.4609375u^4 - \dots. \quad (22)$$

Average Values.

The process of finding the average values of these forces over a long time T, integrating each equation with respect to t between the limits of time 0 and T, and dividing by T, is to multiply each term of the series (22) by the quantities in parentheses and integrate each separately, adding the resulting integrals. It may be shown that the series (22) is rapidly convergent for large values of x_*, y_*, and z_*, due to the factor $\dfrac{2}{s^2}$ in the expression for u (6); and experience has shown that there is no gain in including any terms above the sixth power of the distance. For this reason the next terms of (22) involving the fifth and higher powers of u are not required. It is evident, however, that the number of terms to be integrated arising from the fourth power of u

alone is very large, and were it not for the fact that the definite integrals of so many of them are zero it would be impracticable to employ the process indicated at all. As it is, the resulting equations which have been derived are rather too long to publish here.

Average Translational Force of Atom on Atom.

The next process is to use these integrated equations to derive the force that one atom exerts upon another, each consisting of a single ring of electrons and a positive charge equal and opposite in value to the sum of the charges of all the electrons for a neutral atom, the centre of mass of the positive charge being at the centre of the orbit of the electrons. In so doing we may use the same equations for determining the force that an electron e of the one atom exerts upon the positive charge of the other atom by simply changing the sign of the force because the product $(-e) \times (+e')$ becomes negative, whereas it was positive for two electrons, and by making the radius of the orbit n of the positive charge equal to zero.

We have also to consider the force that each electron e' in the second atom exerts upon the positive charge of the first atom by making the radius m equal to zero. Fortunately, when the three sets of forces so obtained, first, the electrons on electrons; second, the electrons of the one atom on the positive charge of the other atom and the electrons of the other atom upon the positive charge of the one atom; and third, the positive charge of the one atom upon the positive charge of the other, are added together, all the terms involving the even powers of the radii m and n cancel out. This drops a large number of terms and leaves only those containing the product $m^2 n^2$, and gives the final result which applies to any two atoms with certain reservations.

These special cases to which the general results do not apply are those in which each atom has one single electron or two electrons revolving at the same angular velocity in each atom ; for the integral equations differ when the angular velocities are equal. Then the phase angle between the two electrons comes into the account. This limitation, however, is restricted to the case where the rings contain one or two electrons. If there are three or more the phase angle disappears in all terms up to and including the sixth power of the distance, and we obtain precisely the same equations for the force of atom on atom by integrating for synchronous revolution as we get for incommensurable velocities when the number per ring is three or more.

Practically the only special cases we have to study are, therefore, where the two atoms are of the same kind, and where they must have rings with one or two electrons. Hydrogen on hydrogen, containing a single electron in the atom, is one of these exceptions and it has been treated as a special case, the equilibrium position of two hydrogen atoms forming a molecule of hydrogen having been found, as given in a subsequent section.

The general equations for the mechanical force of the second atom A' upon the first atom A, with the exceptions noted, are as follows:—

$$F_x = + \frac{e^2}{Ka_*^2} \left\{ + \frac{a_*^2}{c^2} \sum_P m^2\omega \sum_{P'} n^2\omega' \left[+ 3X\cos\alpha + \cdot 75Z\sin\alpha - 3\cdot 75XY^2\cos\alpha \right. \right.$$

$$- 3\cdot 75X^2Z\sin\alpha - 3\cdot 75X^3\cos\alpha \bigg] v^{-4} - \sum_P m^2 \sum_{P'} n^2 \bigg[+ 9\cdot 375X$$

$$+ 7\cdot 5Z\sin\alpha\cos\alpha + 13\cdot 125X\cos^2\alpha - 13\cdot 125(X^3 + 5XY^2 + 2XZ^2\sin^2\alpha$$

$$+ 5X^3\cos^2\alpha + 7X^2Z\sin\alpha\cos\alpha + Y^2Z\sin\alpha\cos\alpha + XY^2\cos^2\alpha)$$

$$+ 59\cdot 0625(+ X^3Z^2\sin^2\alpha + X^3Y^2 + X^5\cos^2\alpha + XY^2Z^2\sin^2\alpha + XY^4$$

$$\left. \left. + X^3Y^2\cos^2\alpha + 2X^4Z\sin\alpha\cos\alpha + 2X^2Y^2Z\sin\alpha\cos\alpha) \right] v^{-6} \right\} i, \quad . \quad (23)$$

$$F_y = + \frac{e^2}{Ka_*^2} \left\{ + \frac{a_*^2}{c^2} \sum_P m^2\omega \sum_{P'} n^2\omega' \left[+ 3Y\cos\alpha - 3\cdot 75Y^3\cos\alpha - 3\cdot 75XYZ\sin\alpha \right. \right.$$

$$- 3\cdot 75X^2Y\cos\alpha \bigg] v^{-4} - \sum_P m^2 \sum_{P'} n^2 \bigg[+ 20\cdot 625Y + 1\cdot 875Y\cos^2\alpha$$

$$- 13\cdot 125(2X^2Y + 6Y^3 + 2YZ^2\sin^2\alpha + 4X^2Y\cos^2\alpha + 6XYZ\sin\alpha\cos\alpha)$$

$$+ 59\cdot 0625(+ X^2YZ^2\sin^2\alpha + X^2Y^3 + X^4Y\cos^2\alpha + Y^3Z^2\sin^2\alpha + Y^5 + X^2Y^3\cos^2\alpha$$

$$\left. \left. + 2X^3YZ\sin\alpha\cos\alpha + 2XY^3Z\sin\alpha\cos\alpha) \right] v^{-6} \right\} j, \quad . \quad . \quad . \quad (24)$$

$$F_z = + \frac{e^2}{Ka_*^2} \left\{ + \frac{a_*^2}{c^2} \sum_P m^2\omega \sum_{P'} n^2\omega' \left[+ 1\cdot 5Z\cos\alpha + \cdot 75X\sin\alpha - 3\cdot 75Y^2Z\cos\alpha \right. \right.$$

$$- 3\cdot 75XZ^2\sin\alpha - 3\cdot 75X^2Z\cos\alpha \bigg] v^{-4} - \sum_P m^2 \sum_{P'} n^2 \bigg[+ 5\cdot 625Z$$

$$+ 3\cdot 75Z\sin^2\alpha + 7\cdot 5X\sin\alpha\cos\alpha + 1\cdot 875Z\cos^2\alpha - 13\cdot 125(+ X^2Z$$

$$+ 4Y^2Z + Z^3\sin^2\alpha + 3X^2Z\cos^2\alpha + 4XZ^2\sin\alpha\cos\alpha + X^2Z\sin^2\alpha$$

$$+ X^3\sin\alpha\cos\alpha + Y^2Z\sin^2\alpha + XY^2\sin\alpha\cos\alpha) + 59\cdot 0625(+ X^2Z^3\sin^2\alpha$$

$$+ X^2Y^2Z + X^4Z\cos^2\alpha + Y^2Z^3\sin^2\alpha + Y^4Z + X^2Y^2Z\cos^2\alpha$$

$$\left. \left. + 2X^3Z^2\sin\alpha\cos\alpha + 2XY^2Z^2\sin\alpha\cos\alpha) \right] v^{-6} \right\} k. \quad . \quad . \quad . \quad (25)$$

F_x, F_y, and F_z denote the three components of the force along the rectangular axes i, j, and k, referring to the atom A, k being along the line of the axis of rotation of the electrons so that they appear to revolve in the clockwise direction when viewed from the positive side of the axis. j and i are in the plane of its equator, the positive direction of j, along the line of intersection of the equatorial planes of the two atoms, being the vector $k \times k'$. a_* is the unit in centimetres in which all the other distances are expressed, and c is the velocity of light. The summation $\Sigma m^2 \omega$, m being the radius and ω the angular velocity of some electron in the atom A, is to be extended to the P electrons in that atom; and similarly $\Sigma n^2 \omega'$ to the P' electrons in the second atom. X, Y, Z are the direction cosines of the position of the second atom referred to the i, j, and k axes at the centre of the first atom, and α is the angle between the axes of rotation of the two atoms. v is the distance between the centres of the two atoms, measured in a_* units.

Up to this point no particular hypothesis as to the structure of the atom has been introduced. The equations apply as well to the central nucleus theory of the atom as to any other theory where electrons are moving in circular orbits about a common centre. The test of different theories is in the results obtained when numerical values of the different quantities are introduced, especially the radii of the orbits and the frequency of revolution of the electrons.

The nature of the equations shows that they are particularly well adapted to the equal moment of momentum hypothesis for each and every electron, since $\Sigma m^2 \omega$ in the coefficient of v^{-4} is proportional to this moment of momentum, and equal to it if multiplied by the mass of the electron. If we denote by β_* the ratio of the velocity of the electron in hydrogen or in the single electron atom to that of light, and let the unit a_* be the radius of its orbit, and ω_* its angular velocity, then we have for each electron in every atom

$m^2 \omega = n^2 \omega' = \omega_*$, and

$$\Sigma m^2 \omega = \mathrm{P} \omega_*; \quad \Sigma n^2 \omega' = \mathrm{P}' \omega_*; \quad \Sigma m^2 \omega \Sigma n^2 \omega' = \mathrm{PP}' \omega_*^2. \quad (26)$$
$$\mathrm{P} \qquad\qquad \mathrm{P}' \qquad\qquad \mathrm{P} \quad \mathrm{P}'$$

The coefficient $\dfrac{a_*^2}{c^2} \Sigma m^2 \omega \Sigma n^2 \omega'$ in the equation may then be
$\mathrm{P}\quad\mathrm{P}'$
replaced by the quantity $\mathrm{PP}' \beta_*^2$, where β_*^2 is a constant quantity, since $\beta_*^2 = \dfrac{a_*^2 \omega_*^2}{c^2}$. The introduction of this hypothesis therefore makes the equations more easily applicable

to any two atoms. It should be noted that there are no terms in the coefficient of v^{-4} which do not contain the factor β_*^2, whereas there are many such terms in the coefficient of v^{-6}. In fact, the terms containing β_*^2 in this coefficient are added to the terms without β_*^2: and since β_*^2 is a very small quantity, all these β_* terms have been omitted from the coefficient of v^{-6} as they do not affect the value of F in a perceptible degree.

The study of these equations is by no means completed. When the three component forces are resolved along the radius vector joining the centres of the atoms to get the total attraction or repulsion between them, and equated to zero, the result gives the locus of all points where there is no force between the atoms along the radius vector. For any given angle α between the axes of the two atoms we obtain a surface in space surrounding the atom which varies in shape continuously with a change in α. It seems likely that these surfaces possess important mathematical properties, and may prove to be of considerable interest to the mathematician. Only a few of the sections of these surfaces by a plane through the origin have as yet been worked out, but they have proved to be of considerable interest because it has been possible by means of them to demonstrate the complete stability of a simple crystal on the cubic system, such as rock-salt or potassium chloride.

When using the numerical values of β_* and the dimensions of the positive electron given in my theory of the atom, I obtain dimensions for a crystal which agree within the limits of error with the experimental work of Bragg and others and confirm his opinion that there is but a single atom at each corner of the cube in the crystals mentioned. Fig. 1 shows a portion of such a crystal and indicates the direction that the axis of rotation of each atom must assume to produce a stable equilibrium structure. Each axis takes the direction of the long diagonal of some cube in a manner to be described in a subsequent section.

Special Case, $\alpha = 0$.

When the axes of rotation are parallel in the same direction, and $\alpha = 0$, the equations are much simplified. The axes of reference may then be chosen so that the two atoms lie in the i, k or the x, z plane and $y = 0$, also $Y = 0$. Since Y is a factor of F_y, this force vanishes, showing that the total force lies in the i, k plane. The forces may then be resolved along

the radius vector joining the atoms and perpendicular to this vector, giving the simplified equations*

$$F_{along} = +\frac{3}{16}\frac{e^2}{Ka_*^2 v^6}\left\{ +PP'(8-12X^2)\beta_*^2 v^2 \right.$$

$$\alpha=0 \qquad \left. +\underset{P}{\Sigma}m^2\underset{P'}{\Sigma}n^2(-40+200X^2-175X^4) \right\}. \quad . \quad (27)$$

$$F_{perp.} = +\frac{3}{16}\frac{e^2}{Ka_*^2 v^6}\sin 2\lambda\left\{ +4PP'\beta_*^2 v^2 \right.$$

$$\left. +\underset{P}{\Sigma}m^2\underset{P'}{\Sigma}n^2(-40+70X^2) \right\}, \quad . \quad . \quad . \quad (28)$$

where λ is the angle of latitude that the line joining centres of atoms makes with the plane of the equator, and $X = \cos\lambda$. If the force in (27) comes out positive it denotes an attraction between the atoms, a repulsion if negative. If the force in (28) comes out positive it indicates that the second atom is forced in a direction toward the positive pole of the first atom. Equating each force to zero and solving for v, we find

$$\alpha=0 \qquad k_2\beta_* v=\left(\frac{40-200X^2+175X^4}{8-12X^2}\right)^{\frac{1}{2}}, \quad . \quad . \quad . \quad (29)$$

and $\qquad k_2\beta_* v=\frac{1}{2}(40-70X^2)^{\frac{1}{2}}, \quad . \quad . \quad . \quad . \quad . \quad (30)$

where $\qquad k_2=(PP'\div\underset{P}{\Sigma}m^2\underset{P'}{\Sigma}n^2)^{\frac{1}{2}}. \quad . \quad . \quad . \quad . \quad . \quad (31)$

The equations (29) and (30) are plotted as curves in fig. 2 in terms of $k_2\beta_* v$ as radius vector; and since $k_2\beta_*$ is constant for a given pair of atoms these radii are proportional to the actual distance between the atoms. In this case the complete equilibrium surface in space is obtained by revolving all the curves about the axis of the atom A, the k axis, giving a surface of revolution. A surface of revolution is obtained only when the axes of the two atoms are parallel in the same or opposite directions.

The factor $\sin 2\lambda$ in (28) shows that in addition to the points on the curved surface obtained from (30), the perpendicular component force is also zero at all points on the k axis or on the equator, that is in the i, j plane. The arrows in the figure indicate the directions of the along- and perpendicular-forces

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* These identical equations have also been obtained from the instantaneous values of the force when integrated for synchronous rotation, which shows that they are true for either synchronous or non-synchronous rotation.

exerted by the central atom upon the second atom at the position of the arrow. They show that the loop curves above and below the equator are stable positions of equilibrium for small displacements, the force tending to restore the atom to the curve for both the along- and perpendicular-forces. The infinite branches approaching the asymptotes shown by dotted lines are positions of unstable equilibrium for the along-force, the along-force being a repulsion throughout all the shaded region on the chart, and an attraction in the clear regions.

If the loop curve of the along-force intersected that of the perpendicular-force at any point, this point of intersection would be a position of stable equilibrium for all displacements in the i, k plane; but there is no such intersection, and hence no position where *only two* such general atoms unite to form a molecule when the axes are parallel. This statement does not apply to the special cases above noted where there are one or two electrons only in some of the rings.

Special Case, $\alpha = \pi$.

When the axes of the two atoms are parallel but in opposite directions, we obtain equations which differ from (27) and (28) only in the sign of the $\beta_*^2 v^2$ term. This might have been foreseen, by observing that the part of the force arising from the first or electrostatic component is not altered by changing the direction of rotation, but that the magnetic or second component is changed in sign. This case gives instead of (29) and (30)

$$\alpha = \pi \qquad k_2 \beta_* v = \left(\frac{-40 + 200\,X^2 - 175\,X^4}{8 - 12\,X^2} \right)^{\frac{1}{2}}, \qquad . \quad . \quad (32)$$

$$k_2 \beta_* v = \tfrac{1}{2}(-40 + 70\,X^2)^{\frac{1}{2}}. \qquad . \quad . \quad . \quad . \quad (33)$$

The resulting chart in fig. 3 has a very different appearance, due to this change in sign, giving loop curves for both the along and perpendicular components along the equatorial direction instead of along the direction of the axis.

The distances to the maximum points of the loops are in the two cases,

$$\alpha = 0 \begin{cases} \text{distance for along-force,} & k_2\beta_* v = \sqrt{5} & = 2 \cdot 236 \\ \text{,,} \qquad \text{,, perp.-force,} & \text{,,} \quad = \sqrt{10} & = 3 \cdot 162 \end{cases} \begin{array}{l} \text{direction of} \\ \text{axis.} \end{array}$$

$$\alpha = \pi \begin{cases} \text{,,} \qquad \text{,, along-force,} & \text{,,} \quad = \sqrt{3 \cdot 75} = 1 \cdot 936 \\ \text{,,} \qquad \text{,, perp.-force,} & \text{,,} \quad = \sqrt{7 \cdot 5} \; = 2 \cdot 739 \end{cases} \begin{array}{l} \text{direction of} \\ \text{equator.} \end{array}$$

$$\text{Special Case, } \alpha = \frac{\pi}{2}.$$

When the axes of the two atoms are perpendicular to each other the resulting surface is not a surface of revolution, and the section of the surface by a plane containing the axis of the first atom A differs for the different positions of the intersecting plane. Such a section by a plane through the two atoms, the axes of both atoms lying in the plane, is shown in fig. 4 (Pl. XI.). The force equations for atoms so situated are

$$
\begin{aligned}
\text{F}_{\text{along}} &= + \frac{3}{16} \frac{e^2}{Ka_*^2 v^6} \Big\{ -12 \,\text{PP}' \beta_*^2 (\sin \lambda \cos \lambda) v^2 \\
\alpha &= \frac{\pi}{2} \\
&\quad + \Sigma_{\text{P}} m^2 \Sigma_{\text{P}'} n^2 (+20 - 175 \sin^2 \lambda \cos^2 \lambda) \Big\} \quad . \quad . \quad (34)
\end{aligned}
$$

$$
\begin{aligned}
\text{F}_{\text{perp.}} &= + \frac{3}{16} \frac{e^2}{Ka_*^2 v^6} \sin \lambda \Big\{ +8 \text{PP}' \beta_*^2 (\sin \lambda \cos \lambda) v^2 \\
\alpha &= \frac{\pi}{2} \\
&\quad + \Sigma_{\text{P}} m^2 \Sigma_{\text{P}'} n^2 (-20 + 140 \sin^2 \lambda \cos^2 \lambda) \Big\} . \quad . \quad (35)
\end{aligned}
$$

Equating each to zero, we find

$$
\alpha = \frac{\pi}{2} \qquad k_2 \beta_* v = \left(\frac{+20 - 175 \sin^2 \lambda \cos^2 \lambda}{12 \sin \lambda \cos \lambda} \right)^{\frac{1}{2}} \quad . \quad . \quad (36)
$$

$$
k_2 \beta_* v = \left(\frac{+20 - 140 \sin^2 \lambda \cos^2 \lambda}{8 \sin \lambda \cos \lambda} \right)^{\frac{1}{2}}. \quad . \quad . \quad (37)
$$

There are now loop curves of stable equilibrium having their maximum points in a direction at 45° with the i and k axes, besides infinite branches of instability which approach the i and k axes as asymptotes. The maximum distances of these loop curves are

$$
\alpha = \frac{\pi}{2} \begin{cases} \text{Along-force} & k_2 \beta_* v = 1 \cdot 990 \\ \text{Perpendicular-force} & \text{,,} \quad = 1 \cdot 937 \end{cases} \quad \begin{matrix} 45° \text{ with the} \\ \text{axes.} \end{matrix}
$$

If the axis of the second atom A′ is reversed in direction, pointing toward the left instead of to the right as shown, this has the effect of reversing the positive direction of the j axis, since the vector $k \times k'$ is the positive direction of this axis. To keep the cyclic order of the i, j, and k axes correct the i axis must be reversed, which would change the sign of X, and produce the effect of rotating the loop curves into the first and third quadrants instead of leaving them as they are in fig. 4. An additional reversal of the axis of rotation of A has the effect of restoring the loop curves to their original position in the second and fourth quadrants.

Assemblages of Atoms.

It may easily be demonstrated as a general proposition from the force equations (23), (24), and (25) that when the direction of rotation of each atom is reversed, the total force of the one on the other is not changed.

When the axes of the two atoms make other angles with each other than 0, $\frac{\pi}{2}$, and π, the equations are not so simple, and the labour of calculating curves is considerably greater. There are two simple arrangements that may be made with atoms of two different kinds, or of the same kind, using these formulæ, where all the atoms and their axes of rotation lie in the same plane. Fig. 5 shows such an arrangement of two kinds of atoms in rows and columns, adjacent atoms alternating in kind and direction of axes. The formula for the case $\alpha = 0$, the stable equilibrium distance being $k_2 \beta_* v = 2 \cdot 236$, applies to all vertical columns, and for $\alpha = \pi$ and $k_2 \beta_* v = 1 \cdot 936$ applies to all horizontal rows. It is evident that each atom in the plane is rigidly held in its position by the action of all the others. Along a diagonal line the atoms are of the same kind alternating in direction, and the formula where $\alpha = \pi$ applies, showing that although they are not at the stable equilibrium distance the force of any atom upon the central atom is exactly balanced by a corresponding atom on the opposite side of the central atom at the same distance.

The diagram is merely illustrative of the process of building up a solid structure with atoms. Of course the force perpendicular to the plane is shown by the formulæ to be zero, but they also show that for any displacement perpendicular to the plane there is no restoring force, and without other planes of atoms it is evidently an unstable arrangement.

There is another important consideration to be taken into account in any arrangement. There are forces which determine the directions of the axes of rotation independent of any consideration of the translational forces upon the whole atom. These are the third and fourth component forces *, which are magnetic components contributing nothing to the translational force but giving an internal turning moment. These forces acting upon one atom are parallel to the plane of the equator of the second atom, the one taking the direction opposite to the velocity and the other opposite to the

* *Loc. cit.* p. 58.

acceleration of the electron. When the planes of the two atoms are parallel these moments of force evidently vanish; and when the two axes of rotation are not parallel there is a moment of force to restore them to the parallel condition, the moment being a function of the angle between the axes of revolution. In fig. 5 the two adjacent atoms in a horizontal row on either side of a given atom with axis downward each tend to turn the given atom upward, if slightly displaced, while the adjacent pair above and below tend to turn it downward. The sum of the turning moments before displacement is zero; but, unless the two sets of moments after displacement show a restoring moment, there is no stable equilibrium. In fig. 5 it is not evident without calculation that the moments after displacement show stability in the plane, since different formulæ apply and the distances are different. The calculation has not been made.

Another arrangement having all axes and atoms in the same plane is shown in fig. 6. This is based upon the formulæ

where $\alpha = \dfrac{\pi}{2}$. Here there is an arrangement of perfect

squares, the same formulæ applying to all adjacent atoms in both rows and columns. The diagonal atoms have axes in the same straight line alternating in direction, and $\alpha = \pi$. Adjacent atoms along the diagonals have equal and opposite translational effect on the central atom. The moment of the forces to turn the axis by an adjacent horizontal pair of atoms is exactly counterbalanced by an adjacent vertical pair of atoms, the one pair turning clockwise and the other counterclockwise by an equal amount. If the axis of any atom is displaced in the plane of the paper so as to bring it more nearly into the direction of the adjacent vertical pair, the turning moment due to this pair is decreased. At the same time the turning moment of the adjacent horizontal pair is increased, and the sum of the moment is, therefore, in a direction opposite to the displacement, thus proving that the equilibrium is stable for moments.

The adjacent diagonal atoms, however, all four tend to turn the central atom in the same direction as the displacement; but the rate of change of the moment is of the second order of smallness because the axes are nearly parallel, whereas, the rate for adjacent horizontal pairs is a maximum, their axes being at right angles. The total equilibrium for moments is, therefore, stable.

A Cubic Crystal.

If we now attempt to build up a solid by placing such planes one above the other, a possible way is to place an exactly similar plane above this one with all axes reversed, making the odd planes like fig. 6 and the even planes like fig. 7. A different formula applies to the distance between the planes, for, in adjacent atoms $\alpha = \pi$, whereas in the

plane $\alpha = \dfrac{\pi}{2}$, and we do not get a perfect cubic crystal.

It is evidently necessary to seek further for the proper arrangement in a cubic crystal. All three principal planes of atoms mutually perpendicular to each other should be identical in character, a condition which cannot be secured when the axes of all atoms in one plane lie in the same plane. Fig. 1 shows an arrangement of the axes in a cubic crystal[*] that satisfies all the required conditions. All axes of rotation lie along some long diagonal of the cube, and a plane of atoms parallel to any face of the cube is similar to all other such planes parallel to any face. A study of the figure shows that the axes of any two adjacent atoms along an edge of the cube lie in the same plane, namely the plane through the two atoms and through the centre of the cube to or from which the axes point. Moreover, the angle between the directions of the axes of rotation of every two adjacent atoms in the whole structure is the same, equal to $\cos^{-1}\frac{1}{3} = 70° \ 31'\!\cdot\!7$, being the angle between any two adjacent long diagonals of the cube. We have to study only four different sorts of cubes shown in figs. 8 to 11 from which the complete structure may be built. The lower left front corner cube in fig. 1 is like that shown in fig. 8; the next adjacent cube to the right in the front row is like fig. 9; and the cube immediately above this is like fig. 10, and the one just back of that, being the central cube in fig. 1, is like fig. 11. Fig. 8 shows axes of all atoms pointing towards the centre, and fig. 11 all away from it. Fig. 9 shows four axes pointing to the centre of an adjacent cube on one side, and four towards the centre of the corresponding cube on the opposite side; while fig. 10 simply reverses the directions of these arrows. In each of these figures any two adjacent axes of atoms along an edge of the cube lie in the same plane, namely, a plane containing the two diagonally

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[*] Since this paper was communicated it has been found that the axes of rotation of atoms in the odd planes parallel to the hexagon fig. 12 should all be reversed in direction.

opposite parallel edges of a cube. This plane is always perpendicular to one face of the cube and makes angles of $45°$ with each of the other faces.

Equilibrium for Translational Forces.

As far as the translational force upon the atom is concerned, its value for all adjacent atoms along any edge may be found by substituting in the general formulæ (23), (24), and (25) the one set of values $Y=0$, $X=-\dfrac{\sqrt{6}}{3}$, $Z=+\dfrac{\sqrt{3}}{3}$ $\cos \alpha=\dfrac{1}{3}$, $a=70° \ 31' \cdot 7$, which gives the forces

$$F_x=+\frac{e^2}{Ka_*^{\,2}}\left\{ PP'\beta_*^{\,2}(-1\cdot089)v^{-4}+\sum_P m^2 \sum_{P'} n^2(+3\cdot517)v^{-6} \right\} i, \quad (38)$$
$\cos \alpha=\frac{1}{3}$

$$F_z=+\frac{e^2}{Ka_*^{\,2}}\left\{ PP'\beta_*^{\,2}(+\cdot19245)v^{-4}+\sum_P m^2 \sum_{P'} n^2(+1\cdot686)v^{-6} \right\} k. \, (39)$$

Multiplying F_x by X and F_y by Z, and taking the sum to find the total force along the line joining the atoms, we find

$$\underset{\cos \alpha=\frac{1}{3}}{F_v}=+\frac{e^2}{Ka_*^{\,2}}\left\{ PP'\beta_*^{\,2}v^{-4}+\sum_P m^2 \sum_{P'} n^2(-1\cdot90)v^{-6} \right\}. \quad (40)$$

Whence, equating to zero we find the distance for stable equilibrium to be

$$k_2\beta_* v=1\cdot378. \quad . \quad . \quad . \quad . \quad . \quad (41)$$

For the value of k_2 see (31) above.

This result includes both cases where the axes point as in fig. 8 and as in fig. 11, since we have shown above that a reversal of both axes of rotation does not change the force. The same remark applies to figs. 9 and 10, and includes all adjacent atoms along edges throughout the whole structure. This result proves that for a small displacement of any given atom in any direction there is a strong force brought to bear upon it to restore it to this position due to the six face-centred atoms above and below, to the right and left, and to the front and back of it.

This statement does not apply to the other surrounding atoms. They produce a zero resultant translational force, but neither a restoring force nor the opposite for small displacements. It is seen that any pair of atoms adjacent to the given central atom along a diagonal line either of a face or of a cube has axes parallel to each other. The general

formulæ (23), (24), and (25) show that when α remains the same and the direction cosines X, Y, and Z are each reversed, each component and, therefore, the total force changes sign. The force of each and every pair of atoms situated at equal distances along any diagonal line upon the central atom is therefore zero; and this completes the demonstration of equilibrium of the whole for translational forces.

Stable Equilibrium for Translational Forces.

Moreover, the central atom is in stable equilibrium for small displacements. It has already been shown to be stable for the six adjacent face-centred atoms. The restoring force per unit of mass and distance for one such atom may be found by differentiating (40) with respect to v, giving

$$\frac{d\mathrm{F}_v}{dv} = + \frac{e^2}{\mathrm{K}a_*^2} \left\{ -4\mathrm{PP}'\beta_*^2 v^{-5} + 11\cdot4 v^{-7} \sum_{\mathrm{P}} m^2 \sum_{\mathrm{P}'} n^2 \right\}; \quad (42)$$

and substituting the equilibrium distance (41) we get

$$\frac{d\mathrm{F}_v}{dv} = + 3\cdot8 \frac{e^2}{\mathrm{K}a_*^2 v^7} \sum_{\mathrm{P}} m^2 \sum_{\mathrm{P}} n^2. \quad . \quad . \quad (43)$$

For the opposite face-centred atom we get the same value, for a small displacement of the central atom toward the one face-centred atom and away from the other makes the force of each toward the original position, changing sign when passing through the origin. For a pair of such atoms we must then double (43).

It is different with two atoms along a diagonal of the cube, for example. In the case where the axes are all in the same straight line, the atoms being of different kinds, the formula where $\alpha = \pi$ applies, showing a repulsion at all distances. By differentiation of the force equation for $\alpha = \pi$ and addition of those for two adjacent atoms, we show that the rate of change of the force is zero for each pair of such atoms, producing a uniform field of force of zero value at the central atom. This reasoning applies to all the other atoms except the six face-centred adjacent atoms; and we have, therefore, completed the demonstration of stability with the exception of the non-translational forces, which produce only turning moments to control the directions of the axes. These will now be considered.

The Equilibrium of Turning Moments.

It may be shown that the total sum of the turning moments of all the atoms in the structure fig. 1 upon any selected atom is zero, and there is no tendency to turn its axis. Any two atoms tend to turn so that their axes are parallel and the turning moment is a function of the angle α between the axes. The moment of atom "*a*," fig. 12, upon A at the centre is counter-clockwise in the plane *aAtk*, when viewed from *h*. The line A*h* is perpendicular to this plane, and the turning moment of *a* upon A may be represented as the vector A*h*. The moment of the opposite atom *b* whose axis is parallel with *a*'s, being an atom of the same kind at the same distance, is equal to that of *a* and in the same direction. The moment of the pair $a+b$ is then 2A*h*. The moment of *e* on A is such that it is counter-clockwise viewed from *n*, and represented by A*n*, which is perpendicular to the plane *eAot*. The axis of the opposite atom *f* is parallel to *e* at the same distance, and this atom being of the same kind doubles the moment, so that $e+f$ gives 2A*n*. The atom *d* gives a counter-clockwise moment when viewed from *s*, the line A*s* being perpendicular to the plane A*dtp*, and the atom *c* similarly doubles the moment, making that of $c+d$ give 2A*s*. The sum of the three vectors $Ah+An+As$ therefore gives the sum of the turning moments of the atoms *a*, *b*, *c*, *d*, *e*, and *f* upon the central atom A. It is evident that this sum is zero, for these three lines lie in the plane *hlsjnq*, being a hexagon made by sectioning the large cube, and they are, moreover, 120° apart. As they are equal in magnitude their sum is zero.

Now consider the atom *k* upon A. This is represented by the vector A*j*, since viewing from *j* the rotation is counter-clockwise in the plane A*kta*. The four atoms *h*, *i*, *j*, and *k* are similar in kind and have parallel axes. Hence the turning moment of the four is 4A*j*. The effect of *o* on A is represented by A*l*, perpendicular to plane A*ote,* and the four similar atoms *l*, *m*, *n*, and *o* give a moment 4A*l*. The effect of *p* on A is represented by A*q*, perpendicular to plane A*ptd,* and the four atoms *p*, *q*, *r*, and *s* give 4A*q*. Since A*j,* A*l,* and A*q* lie also in the same hexagon and 120° apart, the sum of the moments of *h*, *i*, *j*, *k*, *l*, *m*, *n*, *o*, *p*, *q*, *r*, and *s* is zero. The only remaining atoms are those along a diagonal of the cube. Since these, *t*, *u*, *v*, *w*, *x*, *y*, *z*, and B, are all similar atoms with axes in the opposite direction to that of A the turning moment of them all is evidently zero, though for a small displacement the moments of these would give instability. The control of the position for stability lies with the other atoms.

Stable Equilibrium for Turning Moments.

The stability of the equilibrium may be demonstrated by considering the nearest face-centred atoms *a, b, c, d, e,* and *f.* Suppose the axis of A is slightly displaced in the plane A*eto,* so as to become more nearly parallel with *e* and *f.* The moment of force due to *e* and *f* is diminished and may be represented by the arrow A*n',* a little less than A*n* but in the same direction. The moments due to the other pairs *a, b, c,* and *d* are scarcely affected in magnitude, as the angle between their axes and that of the central atom A is only changed by a comparatively slight amount. The direction of A*h* is slightly rotated out of the plane of the hexagon toward the front side, and of A*s* similarly rotated toward the back side. The resultant of A*h* + A*s* then maintains approximately the same magnitude and direction as before, namely A*l.* The resultant of the moments of the six atoms *a, b, c, d, e,* and *f* after displacement of A is then the sum of A*l* and A*n',* namely AM in the direction of A*l.* The resulting moment AM tends to turn the atom A in the counter-clockwise direction when viewed from *l,* and hence acts against the direction of the small displacement which was in the opposite direction, so as to make A more nearly parallel with *e* and *f.* The original position of the axis of A is, therefore, one of stable equilibrium for such a displacement. Were it displaced in any other direction we would arrive at a similar result. A similar process of reasoning may be applied to the twelve atoms *h, i, j, k, l, m, n, o, p, q, r, s,* arriving at a similar conclusion.

This completes the proof of stability both of the directions of the axes of rotation and the translational position of each and every atom in the whole structure in a cubic crystal. Before giving numerical values of the distances between atoms it seems best to consider a special case, that of the hydrogen molecule.

The Hydrogen Molecule.

Assuming that the two atoms in the hydrogen molecule are alike, each having a single electron revolving at the same speed, we have to find the average force between two synchronously revolving electrons, resolved along the line joining centres. This has been done in a former paper[*] for the case where the axes of rotation are parallel. This gives

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[*] *Loc. cit.* equations (42) and (44). Note an omission in the coefficients, corrected in a note at bottom of page 325, in a subsequent paper, Phil. Mag. vol. xxix. Feb. 1915.

to the sixth power of v when the radii of the orbits are each equal to m in a_* units,

$$F_{1_{along}} = + \frac{ee'}{Ka_*^2} \left\{ -v^{-2} + m^2(1-\Gamma)(3-4\cdot5X^2)v^{-4} + m^4(1-\Gamma)^2(-7\cdot5 + 37\cdot5X^2 - 32\cdot3125X^4)v^{-6} \right\}, \quad . \quad (44)$$

$$F_{2_{along}} = -\beta^2 \Gamma F_{1_{along}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

$$F_{1_{perp.}} = + \frac{ee'}{Ka_*^2} \sin 2\lambda \left\{ 1\cdot5m^2(1-\Gamma)v^{-4} + m^4(1-\Gamma)^2(-7\cdot5 + 13\cdot125X^2)v^{-6} \right\},$$
$$. \quad . \quad . \quad (46)$$

$$F_{2_{perp.}} = -\beta^2 \Gamma F_{1_{perp.}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (47)$$

Here Γ denotes $\cos\gamma$, and γ is the phase difference between the instantaneous positions of the two electrons being considered, and is constant for synchronous rotation. When we add the forces of the two electrons, one in each atom, upon each other, the electrons on the opposite positive charges and the positive on the positive, the force of one hydrogen atom upon another with axes parallel and when γ is zero degrees is

$$F_{along} = \frac{3}{16} \frac{e^2 m^2}{Ka_*^2 v^6} \left\{ + \frac{16}{3}\beta_*^2 v^4 + (-16 + 24X^2)v^2 + m^2(20 - 100X^2 + 87\cdot5X^4) \right\}$$
$$. \quad . \quad . \quad (48)$$

$$F_{perp.} = \frac{3}{16} \frac{e^2 m^2}{Ka_*^2 v^6} \sin 2\lambda \left\{ -8v^2 + m^2(20 - 35X^2) \right\}. \quad . \quad . \quad . \quad . \quad . \quad (49)$$

Stable Equilibrium for Translational Forces in the Hydrogen Molecule.

Equating the along force to zero we find

$$\beta_* v = [1\cdot5 - 2\cdot25X^2 \pm (-1\cdot5 + 2\cdot25X^2)]^{\frac{1}{2}}. \quad . \quad (50)$$

The plot of this curve is shown in fig. 13. Equating the perpendicular force (49) to zero gives $\sin 2\lambda = 0$, denoting the vertical and horizontal axes on the chart. Since the brace in this equation contains no β term there is no curve equating this factor to zero. The values of v obtained from this are very small and have no meaning, since the equations only hold for large values. The series from which it is derived is not convergent for small values. The arrows indicate the directions of the two component forces at various locations on the chart, and show that there is a stable position of equilibrium for the two positions on the axis, one above and the other below the central atom.

Stable Equilibrium for the Phase Difference in the Hydrogen Molecule.

It remains to be shown that when the phase angle γ is zero the two electrons are in stable equilibrium as to phase for small displacements along the orbit. It is, first, evident by considering the instantaneous forces when γ is exactly zero that there is no force to accelerate or to retard the second electron. The static force due to the positive charge of the opposite atom on the electron may be resolved into two, the one perpendicular to the plane of the orbit and the other along the radius of the orbit, neither of which gives any tangential force along the orbit for any position of the electron. The only other force is that due to the second electron upon the first. The instantaneous values of the four components of this force when resolved along the tangent to the orbit is given by equations (53) to (56) of the former paper. These all vanish when $\gamma = 0$ and $x = 0$, as it does when the atom is on the axis, which completes the proof of phase equilibrium of the electrons when $\gamma = 0$.

That the equilibrium is stable may be shown by slightly displacing the second electron along its orbit. The effect of the positive charge gives no force along the orbit as before. We need only consider electron on electron. For small displacement a small component of force is obtained along the tangent for the first, second, and third components of the instantaneous force, but not for the fourth. (See equations (1), (2), (3), and (4) of former paper.) The fourth component depends upon the rate of change of the distance R between the electrons which is zero. The first and second components give respectively

$$F_1 = \frac{e^2}{KR^3} a_* \Delta\gamma, \quad \cdots \quad (51)$$

$$F_2 = -\frac{e^2 \beta_*^2}{KR^3} a_* \Delta\gamma, \quad \cdots \quad (52)$$

where $\Delta\gamma$ is the small displacement angle, a_* the radius of the orbit, and R the distance between electrons, also between atoms. The second force is negligible in comparison with the first because β_*^2 is a small quantity. These two components alone show instability because they tend to increase

the displacement angle $\Delta\gamma$.   The third component[*] gives

$$F_3 = -\frac{e^2\beta_*^2}{KRa_*}\Delta\gamma, \quad . \quad . \quad . \quad . \quad (53)$$

a force tending to restore the electron and produce stability. The ratio of F_3 to F_1 gives

$$\frac{F_3}{F_1} = -\frac{\beta_*^2 R^2}{a_*^2} = -\beta_*^2 v_2. \quad . \quad . \quad . \quad (54)$$

If this ratio exceeds unity when the distance R is that for stable equilibrium of the translational forces, the moments of the forces are also stable.

The distance between the atoms at the position of equilibrium is found by making $X=0$ in (50), which gives, taking the negative sign,

$$\beta_*^2 v^2 = 3 \quad \text{or} \quad v = \frac{\sqrt{3}}{\beta_*}. \quad . \quad . \quad . \quad (55)$$

This proves that the ratio in (54) is equal to three, and that the restoring force of the third component is three times greater than the electrostatic force of the first component. The total restoring force for a small displacement along the orbit is then

$$F = -\frac{2e^2}{KR^3}\Delta s, \quad . \quad . \quad . \quad . \quad . \quad (56)$$

where Δs is the linear displacement.

Vibration Frequencies in the Hydrogen Atom.

We will now find the force with which one hydrogen atom is restored to its original position when displaced along the line joining the atoms.   Let the common centre of mass of the two atoms be taken as origin, a point halfway between the atoms which remains fixed, and let each of the two atoms be displaced to an equal distance away from the origin. The force equation (48) becomes, when $X=0$,

$$F_{\text{along}} = +\frac{e^2}{K}\left\{ +\frac{1}{4}\beta_*^2 x^{-2} - \frac{3}{16}a_*^2 x^{-4} + \frac{3\cdot75}{64}a_*^4 x^{-6} \right\}, \quad (57)$$

where x is the distance in centimetres from the mid-point to one atom.   Differentiating to find the rate of change of the

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[*] The factor $(1+u)^{-\frac{1}{2}}$ was omitted from the text, p. 73, in giving the formula (55), but it appears in the brackets in the alternative value there given.

force, and substituting $x = \dfrac{\sqrt{3}}{2}\dfrac{a_*}{\beta_*}$, the equilibrium distance,

$$\frac{d\mathrm{F}}{dx} = \frac{e^2}{\mathrm{K}}\left(+ \frac{4}{3^{\frac{3}{2}}}\frac{\beta_*^{\frac{5}{2}}}{a_*^{3}} \right), \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (58)$$

omitting the term in x^{-7} as being small.

This expression gives the force acting per unit of distance and per unit of mass. Equating to the mass times the acceleration per unit of distance, we derive the frequency of oscillation

$$n_{\text{along}} = \frac{e\beta_*^{\frac{5}{2}}}{3^{\frac{3}{4}}\pi m^{\frac{1}{2}}a_*^{\frac{3}{2}}}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (59)$$

By a similar process we find from (49) the frequency of vibration of the mass m perpendicular to the line joining the atoms to be

$$n_{\text{perp.}} = \frac{n_{\text{along}}}{\sqrt{2}}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (60)$$

These were published as equations (13) and (15) in a recent paper[*], without the process of derivation.

Comparison of Experimental and Theoretical Values[†].

We are now in a position to use the experimental determinations of the distances between atoms in cubic crystals, and of the frequencies of vibration in the hydrogen atom as determined by the light spectrum, to compare the results of the theory with known experimental values. For many points in the theory reference must be made to a recent paper[‡]. The fundamental constant b, the radius of the

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[*] Phil. Mag. vol. xxix. p. 326, Feb. 1915.

[†] Since this paper was communicated the force of every atom in a cube, of edge four times the length of the elementary cube, upon the central atom has been calculated. There are 26 atoms surrounding the centre in the first cube, and 98 more in the next cube, making a total of 124 atoms besides the central atom. With the central atom there are $125 = 5^3$ atoms. The approximate result in equation (66) has been modified a little by this work so that it comes into good agreement with the atomic theory in (70). A study of monometric crystals of various compounds has made it possible to find the values of Σm^2 characteristic of individual atoms. This is an additional property of the atom itself, as characteristic as the atomic weight or the atomic number, and has proved to be of importance in determining the compounds into which the atom enters. It has in fact made it possible to predict the arrangement of the atoms in some crystals in advance of the published investigation by means of X-rays, and it will prove interesting if these predictions are later confirmed by such a study.

[‡] *Loc. cit.*

positive electron, which is the same as that of the hydrogen atom, is determined from the fact that the number of electrons per gram is constant for any substance, equal to 6×10^{23} approximately, together with the approximation that the volume of all the atoms per gram is 10^{-12} cubic centimetre, the reciprocal of the æther density. This gives

$$b = \cdot 735 \times 10^{-12} \text{ cm.} \quad \ldots \ldots \quad (61)$$

The fundamental constants $\omega_* = 2\pi s$, the angular velocity and frequency of the single electron in the hydrogen atom, are determined from Planck's constant together with the above value of b, to be

$$s = \frac{e^2}{2bh} = 2 \cdot 385 \times 10^{19}, \quad \ldots \ldots \quad (62)$$

where h is Planck's constant, $6 \cdot 5 \times 10^{-27}$, and e the electronic charge $4 \cdot 77 \times 10^{-10}$. Hence

$$\omega_* = 15 \cdot 0 \times 10^{19}. \quad \ldots \ldots \quad (63)$$

The distance between a sodium and a chlorine atom in rock-salt along the edge of a cube is given in a_* units in the theory by (41) above. In centimetres this is

$$l = 1 \cdot 378 \frac{c}{\omega_*} \sqrt{\frac{\sum_P m^2 \sum_{P'} n^2}{PP'}}, \quad \ldots \ldots \quad (64)$$

using the value of k_2 in (31) and writing $\beta_* = \dfrac{a_* \omega_*}{c}$, c being the velocity of light. Equating l to $2 \cdot 814 \times 10^{-8}$ cm., the distance in a rock-salt crystal, we find

$$\sqrt{\sum_P m^2 \sum_{P'} n^2} = 102 \sqrt{PP'}. \quad \ldots \ldots \quad (65)$$

The theory gives for sodium $P = 23$ and for chlorine $P' = 35$, each being equal to the number of electrons in the atom. Hence for sodium and chlorine atoms

$$\sqrt{\sum_{23} m^2 \sum_{35} n^2} = 2895. \quad \ldots \ldots \quad (66)$$

The values of the radii of the orbits of the electrons within the atoms, m for sodium and n for chlorine, are measured in a_* units, where a_* is the radius of the orbit in the single electron atom, hydrogen. We cannot arrive at the theoretical value of the radical in (66) until this unit is determined

in centimetres. A rough approximation to it was given in the former paper, but a more accurate way is to derive it from the hydrogen spectrum, assuming that (59) gives the vibration frequency of the fundamental term in Balmer's series. This may be written

$$n_{\text{along}} = \frac{e}{3^{\frac{3}{4}}\pi m^{\frac{1}{2}}}\left(\frac{\omega_*}{c}\right)^{\frac{5}{2}} a_*. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (67)$$

All the quantities in the right member of this are known except a_*. Hence, by equating the frequency to $\cdot 823 \times 10^{15}$, the constant in Balmer's series, we find a_*,

$$a_* = \cdot 207 \times 10^{-12} \text{ cm.}$$

and

$$\beta_* = \frac{a_*\omega_*}{c} = \cdot 00103. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (68)$$

The value of this unit in the former paper, determined in a different way, was $\cdot 285 \times 10^{-12}$ cm. From (63) and (68) the universal constant angular moment of momentum of every electron is seen to be

$$m\omega a^2 = \cdot 564 \times 10^{-32}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (69)$$

185,000 times smaller than the value of this constant given by Bohr's theory[*] of the central nucleus atom.

If we assume that the electrons are distributed in a chlorine atom according to the scheme shown in fig. 3 of the former paper[†], having rings of 16, 12, 6, and 1 electrons, and also that the positive charge has a spherical shape, its radius is $2\cdot 4 \times 10^{-12}$ cm., or $\dfrac{2\cdot 4}{\cdot 207} = 11\cdot 6\, a_*$ units. Taking $n_0 = 11$, $n_1 = 7\cdot 5$, $n_2 = 5$, and n_3 negligible, we find $\underset{35}{\Sigma n^2} = 2800$ approximately. The electrons in the sodium atom are not shown in the figure referred to, but the radius of the positive charge is $2\cdot 09 \times 10^{-12}$ cm., $= 10\cdot 1 a_*$ units. An estimate of the positions of the electrons in three rings 13, 8, and 2, gives about 1500 as the value of Σm^2 for sodium. The theoretical value is, therefore, approximately

$$\sqrt{\underset{23\quad 35}{\Sigma m^2 \Sigma n^2}} = 2050, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (70)$$

which is to be compared with 2895 in (66). It is needless to say that these figures are in agreement within the limits

[*] N. Bohr, Phil. Mag. July 1913, vol. xxvi. p. 15.
[†] *Loc. cit.* p. 323.

of error of our knowledge of the distribution of the electrons. If the radius of the outside ring of electrons in chlorine were about 13 instead of $11a_*$ units above, and that in sodium about 11 instead of 10, this would make the values in (69) and (66) agree.

There are many fundamental questions that have probably suggested themselves to those who have followed the subject here presented; and the belief that they will receive a satisfactory answer increases with the progress of the work. Other forms of crystals than the cubic system must be explained, as well as the combinations of elements known to chemistry. This latter, of course, need not be restricted to the neutral atom, but the former most likely is. It is probable that alternative forms of stable crystals will be found with the same combinations of atoms, and the most stable of these is likely to be the one that exists in nature, though sometimes there may be more than one.

One important matter that should be emphasized is made evident by a study of the cubic crystal in fig. 1. There is the same number of chlorine atoms in rock-salt that have their axes pointing in any given direction as in the exact opposite direction, and so of sodium. The total magnetic effect of the crystal is, therefore, very small. Were this not the case, and if there were an excess in one direction more than another, there would be an aggregate giving a strong unbalanced magnetic force, and the crystal would be magnetic. It is to be noticed that the magnetic component in this crystal varies as the inverse fourth power of the distance from the atom while the electrostatic varies as the sixth power. At great distances, therefore, only the magnetic force can prevail, the electrostatic being a negligible quantity in comparison; and if the axes of the atoms are so turned on the whole as to cancel their magnetic components, the structure is non-magnetic.

The ability to magnetize the substance by an outside force must depend upon the degree of stability of the turning moments which have been considered in detail in the paper. It is quite possible that in iron we have a peculiar case where the translational equilibrium is very stable, but the turning moments are in almost neutral equilibrium. Such a condition will explain the unique properties of iron, nickel, and cobalt.

The fact that the action between two magnetic poles in iron is inversely as the square of the distance instead of

inversely as the fourth power of the distance, seems to show that the atom of iron must come under one of the special cases above mentioned, having a centre ring with only one or two electrons. The force in this case may be inversely as the square of the distance. This is shown by the equations for the hydrogen atom, (48) and (49) above, where the first term due to the magnetic force contains the inverse second power of the distance, showing that for hydrogen atoms at a great distance, having parallel axes, the attraction is inversely as the square of the distance. This suggests that possibly the rings of electrons in fig. 3 * of the former paper are correct, for there iron and cobalt have a single central electron, and nickel two central electrons, which will give rise to the same law of variation of the force with the distance as that in hydrogen.

In this paper the positive charge in each atom is supposed to be at rest free from vibration of its whole mass, and long waves of radiant heat are attributed to the vibration of this mass. The period of this vibration in the hydrogen molecule was given in the former paper. It should be considered, therefore, that the work in this paper applies to the state of matter at the absolute zero of temperature.

LXXXI. *On the Principal Series in the Spectra of the Alkali Metals. By* W. Marshall Watts, *D.Sc.*†

IN the Philosophical Magazine for 1908 (xvi. p. 945) Wood describes the absorption spectrum of sodium vapour in which he measured 48 lines of the principal series forming the most extended " Balmer series " hitherto observed.

Bevan ‡ applied Wood's method to the other alkali metals, and observed extended series in lithium, potassium, rubidium, and cæsium. He also discusses the representation of these long series by formulæ, obtaining very close results by the use of the formula employed by Mogendorff in 1906 and by Hicks in 1910, viz.,

$$O.F. = C.F. - \frac{109675}{\left(m + \mu + \dfrac{c}{m}\right)^2}.$$

* *Loc. cit.*
† Communicated by the Author.
‡ Proc. Roy. Soc. lxxxiii. p. 423 (1910), lxxxiv. p. 209, lxxxv. pp. 54, 55, lxxxvi. p. 300 (1911).

The Principal Series in Sodium.

| Observed | | | | | | m. | Calculated. | Observed—Calculated. | | | |
Kayser & Runge.	Eder & Valenta.	Exner & Haschek. (Arc)	Exner & Haschek. (Spark)	Schillinger. (Spark)	Wood. (Absorption)				Birge.	Hicks.	Lohuizen.
5896·16	5896·15	5896·17	5896·18	5896·16		2	5896·16	-·01	0	0	0
5890·19	5890·18	5890·20	5890·21	5890·19			5890·19	0			
3303·07	3303·12	3303·11	3303·17	3303·16		3	3303·07	+·06	0	0	-·01
3302·47	3302·50	3302·56	3302·52	3302·49			3302·47	+·04			
2852·91	2852·91	2853·00	2852·9	2853·00	2852·91	4	2853·04	0	-·04	0	0
							2852·84				
2680·46	2680·46	2680·50			2680·46	5	2680·39	+·05	+·09	+·03	+·11
2593·98	2593·98				2594·05	6	2593·89	+·09	+·09	+·02	+·11
2543·85					2543·82	7	2543·86	-·03	-·05	-·09	0
2512·23					2512·15	8	2512·16	+·03	+·07	-·01	0
					2490·70	9	2490·74	-·04	-·04	-·13	-·04
					2475·60	10	2475·56	+·04	+·03	-·07	+·03
					2464·53	11	2464·42	+·11	+·10	+·01	+·11
					2456·02	12	2455·97	+·05	+·05		+·04
					2449·46	13	2449·42	+·04	+·04		+·03
					2444·24	14	2444·23	+·01	-·03		0
					2440·06	15	2440·06	0	+·01		0
					2436·70	16	2436·64	+·06	+·06	-·05	+·05
					2433·85	17	2433·82	+·03	+·04		+·03
					2431·43	18	2431·45	-·02	-·01		+·02
					2429·42	19	2429·44	-·02	-·02		-·03

λ	n	λ	(o−c)	(o−c)	(o−c)	(o−c)
2427·72	20	2427·73	−·01	−·01	−·10	−·02
2426·28	21	2426·26	+·02	+·02		+·01
2425·00	22	2424·99	+·03	+·01		0
2423·88	23	2423·88	+·01	0		−·01
2422·90	24	2422·90	0	0	−·09	−·01
2422·04	25	2422·04	0	0		−·01
2421·29	26	2421·29	+·02	0		0
2420·60	27	2420·59	+·01	+·01		−·01
2420·02	28	2420·00	+·04	+·02	−·17	+·02
2419·50	29	2419·45	+·07	+·05		+·05
2419·00	30	2418·96	+·06	+·04		+·04
2418·44	31	2418·51	−·05	−·07		−·07
2418·09	32	2418·11	0	−·02		−·02
2417·71	33	2417·74	−·01	−·03	−·10	−·02
2417·38	34	2417·40	+·01	−·02		−·02
2417·10	35	2417·09	+·02	−·01		−·01
2416·80	36	2416·81	0	−·01		−·01
2416·56	37	2416·55	+·03	+·02	−·09	+·01
2416·33	38	2416·31	+·04	+·02		+·02
2416·11	39	2416·09	+·03	−·01		+·02
2415·89	40	2415·88	+·02	−·01		+·02
2415·70	41	2415·69	+·03	+·02		+·01
2415·52	42	2415·50	+·02	+·02	−·07	+·01
2415·37	43	2415·35	+·03	+·02		+·02
2415·21	44	2415·19	+·04	+·01		+·02
2415·06	45	2415·05	+·03	+·03		+·02
2414·94	46	2414·91	+·05	−·01		+·02
2414·78	47	2414·79	+·01	−·03	−·16	−·01
2414·64	48	2414·67	−·01	−·03		−·01
2414·50	49	2414·56	−·04	−·06		−·06

Birge has the convergence-frequency 41448·71, Hicks 41446·76, and von Lohuizen 41448·5.

Other formulæ which have been employed (besides that of Kayser and Runge, which is not sufficient) are the Ritz form

$$O.F. = C.F. - \frac{109675}{\left(m + \mu + \dfrac{c}{m^2}\right)^2},$$

and that of Lohuizen

$$O.F. = C.F. - \frac{109675}{\left(m + \mu + \dfrac{c}{O.F.}\right)^2}.$$

A comparison of the results given by these different formulæ is calculated to afford useful guidance in the examination of less extended series.

The case of Sodium has been examined at length by Birge [*], who gives wave-lengths on the Fabry and Perot scale reduced to vacuum, and employs the Ritz formula with 109678·6 as the value of N instead of 109675.

In the table on pp. 776–7 I give the wave-lengths calculated from the formula

$$O.F. = 41448·67 - \frac{109675}{\left(m + ·147408 - \dfrac{·031328}{m-1}\right)^2}$$

for the less refrangible component, and

$$O.F. = 41448·67 - \frac{109675}{\left(m + ·148204 - \dfrac{·031380}{m-1}\right)^2}$$

for the more refrangible component of the pairs of lines.

In Potassium the formulæ

$$O.F. = 35005·56 - \frac{109675}{\left(m + ·293076 - \dfrac{·061356}{m-1}\right)^2},$$

$$O.F. = 35005·56 - \frac{109675}{\left(m + ·296228 - \dfrac{·061628}{m-1}\right)^2}$$

give the following values :—

[*] Astrophys. Journ. xxxii. p. 112 (1910).

The Principal Series in Potassium.

Observed.					m.	Calculated.	Observed—Calculated.		
Ramage. (Flame.)	Exner & Haschek. Arc.	Exner & Haschek. Spark.	Schillinger.	Kayser & Runge. Arc.				Birge.	Hicks.
{ 7697 { 7664			{ 7699·41 { 7665·56	{ 7969·3 * { 7665·6	2	{ 7699·10 { 7665·60	+·4 −·25	0	−4 −4·6
{ 4047·39 { 4044·33	{ 4047·42 { 4044·36	{ 4047·30 { 4044·30	{ 4047·35 { 4044·31	{ 4047·36 † { 4044·29	3	{ 4047·51 { 4044·13	−·11 +·19	+·01	0 0
{ 3447·56 { 3446·55	{ 3447·54 { 3446·51	{ 3447·6 { 3446·60	{ 3447·52 { 3446·53	{ 3447·49 { 3446·49	4	{ 3447·59 { 3446·56	+·07 −·02	+·04	0 0
{ 3217 { 3217·36	3217·75	3217·3	3217·54	{ 3217·76 { 3217·27	5	{ 3217·83 { 3217·36	−·07 −·09	−·02	0 +·02
	Eder & Valenta. 3102·3		3103·05	{ 3102·37 { 3102·15	6	{ 3102·27 { 3102·00	+·10 +·15	+·08	+·21 +·18
				3034·94	7	{ 3035·09 { 3035·00	−·10	−·26	0
	2992·3	2992·4	2992·47	2992·33	8	2992·43	+·03	−·19	+·01
			2963·37	2963·36	9	2963·53	−·16	−·25	−·06
				2942·8	10	2942·99	−·19	−·27	−·09
				Bevan. Absorption.					
				2928·0	11	2927·86	+·14	+·07	
				2916·6	12	2916·38	+·22	+·16	
				2907·6	13	2907·45	+·15	+·09	
				2900·4	14	2900·38	+·02	−·02	
				2894·6	15	2894·67	−·07	−·10	
				2889·7	16	2890·00	−·30	−·32	
				2885·9	17	2886·12	−·22	−·25	
				2882·9	18	2882·87	+·03	0	
				2880·3	19	2880·12	+·18	+·15	
				2877·9	20	2877·77	+·13	+·09	
				2875·8	21	2875·75	+·05	+·01	
				2874·1	22	2873·99	+·11	+·07	
				2872·5	23	2872·46	+·04	0	
				2871·1	24	2871·12	−·02	−·04	
				2870·0	25	2869·93	+·07	+·05	

* { 7699·32
 { 7665·29 Hermann. { 7699·08
 { 7664·91 Saunders. { 7699·41
 { 7665·39 Eder & Valenta. { 7701·92
 { 7768·54 Lehmann.

† { 4047·571
 { 4044·599 Jewell. { 4047·4
 { 4044·3 Eder & Valenta.

Birge has convergence-frequency 35005·29, and Hicks 35006·21.

For Rubidium, the formulæ

$$\text{O.F.} = 33688 \cdot 20 - \frac{109675}{\left(m + \cdot 352806 - \dfrac{\cdot 073542}{m-1}\right)^2},$$

$$\text{O.F.} = 33688 \cdot 20 - \frac{109675}{\left(m + \cdot 365934 - \dfrac{\cdot 073868}{m-1}\right)^2}$$

give the following results :—

The Principal Series in Rubidium.

Flame. Eder & Valenta.	Arc. Lehmann.	Arc. Saunders.	Spark. Exner & Haschek.	Kayser & Runge. (Arc.) / Bevan. (Absorption.)	m.	Calculated	Birge.	Hicks.	Bevan.
7950·4	7950·46	7947·6		7950	2	7949·03	+·01	0	
7806·2	7805·98	7800·2		7811*		7803·13	+·04	-2·5	
Ramage.		Exner & Haschek.							
4215·63		4215·75	4215·73	4215·72	3	4215·72	-·01	0	0
4202·04		4202·06	4201·97	4201·98		4201·99	+·01	0	
3591·86		3591·74		3591·74	4	3591·74	+·04	+·20	0
3587·27		3587·21		3587·23		3587·22	+·02		0
3350·98		3351·00		3351·03	5	3350·94	+·06	+·16	0
3348·84		3348·89		3348·86		3348·93	-·07		+ ·06
3229·26					6	3229·27	-·01	-·01	+ ·02
3228·18						3228·10	+·08		- ·04
				Bevan. (Absorption.)					
				3158·25†	7	3158·39	+·08	-·22 +1·00	-·19
				3157·69		3157 67	+·02	+ ·27	-·03
				3112·95	8	3112·95	0	-·23	-·11
				3082·39	9	3082·34	+·05	-·65	+·01
				3060·62	10	3060·56	+·06	-·41	-·01
				3044·33	11	3044·47	-·14	-·40	-·20
				3032·20	12	3032·25	-·05	-·26	-·11
				3022·70	13	3022·74	-·04	-·23	-·09
				3015·16	14	3015·20	-·04	-·18	-·11
				3009·03	15	3009·11	-·08	-·08	-·15
				3004·11	16	3004·12	-·01	-·27	-·08
				2999·96	17	2999·98	-·02	-·03	-·08
				2996·51	18	2996·51	0	-·26	-·06
				2993·52	19	2993·57	-·05	-·21	-·12
				2991·12	20	2991·06	+·06	-·09	+·01
				2988·94	21	2988·89	+·05	-·13	-·01
				2987·01	22	2987·02	-·01	-·14	- ·06
				2985·45	23	2985·38	+·07	0	+·02
				2984 05	24	2983·94	+·11	+·14	+·06
				2982·68	25	2982 67	+·01	+·41	-·05
				2981·51	26	2981·53	-·02	+·53	-·08
				2980·52	27	2980 53	-·01		-·07
				2979·62	28	2979·62	0		-·07
				2978·81	29	2978·81	0		-·07
				2978·10	30	2978·08	+·02		-·05
				2977·39	31	2977·42	-·03		-·09

* {7947·7 / 7800·3} Eder & Valenta (Arc).   † 3158·7 Saunders.

Birge has the convergence-frequency 33687·82, Hicks 33687·50, and Bevan 33687·5.

For Cæsium the formulæ

$$\text{O.F.} = 31404\cdot31 - \frac{109675}{\left(m + \cdot418202 - \dfrac{\cdot090052}{m-1}\right)^2},$$

$$O.F. = 31404\cdot31 - \cfrac{109675}{\left(m + \cdot449969 - \cfrac{\cdot089326}{m-1}\right)^{2}}$$

give the following results :

The Principal Series in Cæsium.

Columns 1–6 are grouped under the heading **Observed.**; the residual columns **Bevan.** and **Hicks.** are grouped under **Observed−Calculated**.

Randall. (Arc.)	Lehmann. (Arc.)	Kayser & Runge. (Arc.)	Exner & Haschek. (Arc.)	Ramage. (Flame.)	Bevan. (Absorption.)	m.	Calculated	Observed−Calculated	Bevan.	Hicks.
8945·0 / 8522·4	8949·92 / 8527·72					2	8949·92 / 8527·72			0
		4593·34 / 4555·44	4593·29 / 4555·34	4593·30 / 4555·46		3	4593·19 / 4555·29			−·02 / +·04
		3888·83 / 3876·73	3889·1 / 3876·7	3888·75 / 3876·31	3888·80 / 3876·53	4	3888·66 / 3876·34	+·04 / +·17		+·42
		3617·08 / 3611·84		3617·49 / 3611·70	3617·56 / 3611·70	5	3617·31 / 3611·54	+·13 / +·05		−·09 / −·22
				3477·25	3480·28 / 3477·03	6	3480·09 / 3476·88	+·19 / +·15	+·09 / −·10	−·05
				3398·40	3400·13 / 3398·27	7	3400·05 / 3398·06	+·08 / +·21	0 / +·13	−·14
				3348·72	3348·84 / 3347·56	8	3348·93 / 3347·63	−·09 / −·07	−·09 / −·12	+·67
				3314	3314·16 / 3313·28	9	3314·18 / 3313·26	−·02 / +·02	−·09 / −·05	+·30
				3287	3289·25 / 3288·68	10	3289·43 / 3288·76	−·18 / −·08	−·25 / −·16	−2·1
					3270·66	11	3271·14 / 3270·64	+·02	−·16	
					3256·77	12	3257·25 / 3256·86	−·09	−·15	
					3246·02	13	3246·43 / 3246·12	−·10	−·16	
					3237·58	14	3237·83 / 3237·58	0	−·07	
					3230·69	15	3230·88 / 3230·68	+·01	−·09	
					3225·11	16	3225·20 / 3225·03	0	0	
					3220·34	17	3220·40	−·06	−·09	
					3216·45	18	3216·46	−·01	−·03	
					3213·02	19	3213·11	−·09	−·09	
					3210·18	20	3210·25	−·07	−·08	
					3207·78	21	3207·78	0	−·02	
					3205·64	22	3205·63	+·01	−·02	
					3203·80	23	3203·76	+·04	+·01	
					3202·13	24	3202·12	+·01	−·02	
					3200·71	25	3200·66	+·05	+·01	
					3199·45	26	3199·37	+·08	+·03	
					3198·25	27	3198·22	+·03	−·01	
					3197·28	28	3197·19	+·09	+·05	
					3196·20	29	3196·27	−·07	−·11	
					3195·42	30	3195·43	−·01	−·05	
					3194·59	31	3194·67	−·08	−·13	
					3193·24	32	3193·98	−·04	−·10	

In the case of Lithium the results are not quite so satisfactory. Hicks finds the convergence-frequency to be $43482 \cdot 20 \pm 1 \cdot 18$. Bevan uses $43482 \cdot 98$, but points out that his latest measurements indicate a higher convergence-frequency.

In the following table I give the results calculated from

$$\text{O.F.} = 43485 \cdot 18 - \frac{109675}{\left(m - \cdot 04929 + \dfrac{\cdot 008185}{m-1}\right)^2}$$

The Principal Series in Lithium.

Flame.	Arc.		Spark.		Absorption.		Calculated.	Observed--Calculated.		
Ramage.	Kayser & Runge.	Exner & Haschek.	Eder & Valenta.	Exner & Haschek.	Bevan.	m.		Bevan.	Hicks.	Birge.
6708·0	6708·2	6708·10	6708 07	6708·09		2	6707·94 +·06	0	0	0
3232·82	3232·77	3232·8	3232·98	3232·80		3	3232·89 −·09	0	0	0
2741·43	2741·39	2741·37	2741·57	2741·32		4	2741·34 +·08	0	+·07	−·07
	2562·60					5	2562·44 +·16	+·07	0	−·01
	2475·13					6	2475·15 −·02	−·11	+·20	−·23
	2425·55					7	2425·52 +·03	−·08	+·01	−·19
	2394·54					8	2394·46 +·08	−·02	+·03	−·15
					2373·9	9	2373·65 +·25	+·09	+·10	0
					2359·4	10	2359·03 +·37	+·22	+·22	+·15
					2348·5	11	2348·33 +·17	+·03		
					2340·5	12	2340·27 +·23	+·08		
					2334·3	13	2334·04 +·26	+·12		
					2329·0	14	2329·12 −·12	−·28		
					2325·2	15	2325·17 +·03	−·13		
					2321·9	16	2321·97 −·07	−·20		
					2319·3	17	2319·31 −·01	−·15		
					2317·1	18	2317·08 +·02	−·12		
					2315·2	19	2315·21 −·01	−·15		
					2313·6	20	2313·61 −·01	−·15		
					2312·2	21	2312·23 −·03	−·17		
					2311·1	22	2311·04 +·06	−·08		
					2310·0	23	2310·01 −·01	−·15		
					2309·0	24	2309·10 −·10	−·24		
					2308·3	25	2308·30 0	−·14		
					2307·5	26	2307·59 −·09	−·23		
					2306·90	27	2306·96 −·06	−·18		
					2306·48	28	2306·39 +·09	−·03		
					2305·87	29	2305·88 −·01	−·11		
					2305·41	30	2305·42 −·01	−·11		
					2304·99	31	2305·01 −·02	−·11		
					2304·63	32	2304·63 0	−·15		
					2304·29	33	2304·30 −·01	−·10		
					2304·00	34	2303·99 +·01	−·07		
					2303·73	35	2303·70 +·03	−·06		
					2303·46	36	2303·44 +·02	−·12		
					2303·24	37	2303·20 +·04	−·05		
					2303·03	38	2302·98 +·05	−·03		
					2302·83	39	2302·77 +·06	−·03		
					2302·59	40	2302·58 +·01	−·08		
					2302·38	41	2302·41 −·03	−·12		
					2302·20	42	2302·24 −·04	−·13		

If we take the mean observed value of the first line 6708·12, which corresponds to the oscillation-frequency 14903·26 *in vacuo,* and, applying the Rydberg–Schuster rule, add 28579·71, Hicks's mean value for the convergence-frequency of the subordinate series, we obtain 43482·97 for the convergence-frequency of the principal series.

LXXXII. *Ionization by Positive Rays.*
By Norman Campbell[*].

1. THE chief facts concerning the ionization of gases by electrons seem to be now thoroughly established, but comparatively little is known concerning ionization by the impact of atoms except when the atoms are those constituting α-rays. The first direct attack on this problem is described in the recent papers of v. Bahr and Franck [†] and of Pawlow [‡], who come to the surprising conclusion that the positively charged particles from hot platinum and hot phosphates can ionize gases when their energy is less than that required by electrons. This result is of the greatest importance for theories of the structure of the atom, for it would seem to indicate that the "ionization potential" for electrons has not the fundamental significance which has often been attributed to it ; it appears that further experiments, especially on the variation of the ionizing power of positive particles with their speed, energy or charge, are desirable.

It is not easy to conduct such quantitative experiments on a gas, into which rays of such low speed as are here considered have practically no power of penetration. But recent work has tended to show § that the liberation of electrons, which takes place when ionizing rays of any kind fall on a metal surface, varies with the properties of those rays in precisely the same manner as the ionization which the rays cause in a gas. Indeed it is highly probable that, when the surface of the metal has been recently polished, the electrons are actually liberated from a layer of gas on the surface of the metal. Experiments on such metal surfaces are free from many of the difficulties which attend experiments on ionization in a gas which has any appreciable volume.

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[*] Communicated by the Author.

[†] E. v. Bahr and J. Franck, *Deutsch. Phys. Gesell. Verh.* xvi. 1. p. 57 (1914).

[‡] W. Pawlow, Roy. Soc. Proc. A. vol. xc. p. 398 (1914).

§ See, *e. g.*, N. Campbell, Phil. Mag. June 1913, p. 803, and March 1915, p. 369.

2. The liberation of electrons at metal surfaces under the action of positive rays has been studied, under the name of "secondary cathode radiation," by several investigators. The only investigations which seem to throw any light on the number of electrons which are liberated by each positive ray are those of Füchtbauer [*], Baerwald [†], and Koenigsberger and Gallus [‡]. Füchtbauer found that when positive rays (probably hydrogen) with an energy of from 31,300 to 15,000 volts fell on a copper plate, the number of electrons liberated by each positive particle varied from 1·36 to 0·89, while the proportion of the positive particles reflected varied from 0·083 to 0·15. Baerwald, using positive rays of hydrogen and helium falling on an aluminium plate, found that the number of electrons liberated by each particle did not change appreciably between 30000 volts and 900 volts, but that the ionizing action ceased abruptly at this lower limit. Koenigsberger and Gallus found that the number of electrons liberated from brass by positively charged rays, of which the nature and speed were not precisely determined, lay between 2 and 4.

Finally Bumstead [§], working with α-rays, found that the variation of the ionizing power of the rays at a metal surface varied with the speed in almost exactly the same manner as the ionizing power in a gas. Hauser [‖], in agreement with other workers, finds the number of electrons liberated at a metal surface by each α-ray to be about 60.

3. In the experiments about to be described, which were conducted in an apparatus of which the essential portion is shown diagrammatically in fig. 1, the positive particles were not (as in the work just mentioned) those of these canal-rays, but those liberated from heated phosphates as in the work of v. Bahr and Franck and of Pawlow. The use of such particles is necessary if their effect is to be investigated for very low potentials at which a discharge will not pass ; it has the additional advantage, even at higher potentials, that the observations can be made in a very low vacuum and the ionization completely localised at the metal surface ; it has the disadvantage that greater uncertainty exists as to the nature of the particles. The particles liberated at the heated strip S, which was of platinum coated either with sodium

* C. Füchtbauer, *Phys. Zeit.* vii. p. 153 (1906).

† H. Baerwald, *Ann. d. Phys.* xli. p. 643 (1913).

‡ J. Koenigsberger u. A. Gallus, *Deutsch. Phys. Gesell. Verh.* xvi. 4. p. 190 (1914).

§ H. A. Bumstead, Phil. Mag. xxii. p. 907 (1911).

‖ Hauser, *Phys. Zeit.* xii. p. 466 (1911).

phosphate or a mixture of sodium and aluminium phosphates, passed through the tube T with an energy corresponding to the difference of potential (V) between S and A, and fell on the copper plate C at the same potential as A.

Fig. 1.
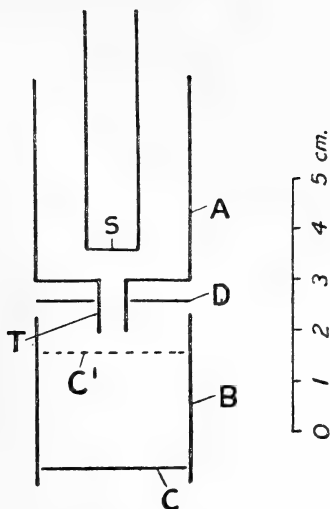
The reflected rays and the electrons liberated at C fell on the cylinder B and plate D, which were coated with soot to avoid further reflexion.

All the portion of the apparatus shown was enclosed in a glass tube, covered with metallic foil to avoid electrostatic disturbances and exhausted by connexion through a wide tube to charcoal immersed in liquid air throughout the observations.

The values of V between 0 and 400 volts were obtained from cells ; no higher potential from this source was available. From 2000 volts upwards they were obtained either from an influence-machine or an induction-coil. With the machine, V was varied by varying a high resistance placed as a shunt across its terminals ; with the coil, V was varied by varying the current in the primary, a unidirectional secondary current being secured by the use of the usual valves. V, when not greater than 400 volts, was read on a voltmeter ; the higher values were determined by means of a spark-gap between balls of 2 cm. diameter, the readings of

the spark-gap being interpreted by the tables given by Landolt and Börnstein.

The current was measured by the method, adopted in all my recent work, which depends on the use of an electrometer and a high resistance. It was always of the order of 10^{-12} amp.; if it was steady, it could be easily measured to 1 part in 1000.

4. Let I_1 be the positive current carried to C by the primary positive particles, I_2 and I_3 the positive currents carried away from it by the reflected positive particles and the liberated electrons respectively. Then $R = I_2/I_1$ will be termed the reflexion coefficient of the rays, $P = -I_3/I_1$ will be termed their ionizing power. If the incident positive particles carry each a single electronic charge, then P will be the average number of electrons produced by each positive particle.

If i_1 is the current received by B, C, and D connected together, then $i_1 = I_1$. If i_2 is the current received by C when B and D, connected together, are kept at a potential slightly higher than that of C, so that all the electrons liberated at C, as well as the reflected primary particles, are absorbed in B and D, then $i_2 = I_1 - I_2 - I_3$. If, on the other hand, B and D are kept at a potential lower than C, the difference of potential being greater than that of the fastest electrons liberated at C, then none of the electrons can leave C and $i_3 = I_1 - I_2$. These statements will be true only if the difference of potential (v) between B and C is not great enough to alter the path of the primary or reflected positive particles. An examination of the relation between i_2 or i_3 and v shows that, if V was not less than 400 volts, this condition could be fulfilled to a high degree of accuracy. In measuring i_2 and i_3, v was $+4$ and -40 volts respectively; any uncertainty in P in the results owing to the condition not being fulfilled exactly certainly does not amount to more than 2 per cent. We may then take

$$P = \frac{i_2 - i_3}{i_1},$$

$$R = \frac{i_1 - i_3}{i_1}.$$

When V is less than 400 another method of measuring P was adopted. C was pushed forward till it occupied the position C' indicated by the dotted lines. D was maintained at a potential 400 volts higher than that of A, B, and C', which were all at the same potential. This difference of potential was, of course, sufficient to ensure that no reflected rays fell on D; it appeared from preliminary experiments

that it was also sufficient to ensure that all the electrons liberated at C′ were absorbed in D. If i_4 is the current which with this arrangement is received by D, then $i_4 = I_3$ and $P = -i_4/i_1$. i_1 was measured as before by withdrawing the plate to C. No precise measurements of R could be made in this case, but everything pointed to it being not greater than 0·02.

5. For values of V which were obtainable by means of cells, the homogeneity of the rays was investigated by noting the variation of i_1 when the potential of B, C, and D was varied relative to A. It was found that, when B, C, D were raised from the potential of A to very nearly that of S the value of i_1 did not decrease 10 per cent.; accordingly at least 90 per cent. of the rays entering B and striking C must have had an energy not differing by more than 1 or 2 volts from V. Similar experiments were difficult when the influence-machine or induction-coil were used to obtain V, for the potential obtained in this manner is not perfectly steady; their variations caused large induced currents in C. But there is no reason to suppose that if a small steady value of V gives homogeneous rays, a large steady value should give heterogeneous rays—so long, of course, as there is no sign of an ordinary discharge passing between S and A. The current between S and A was approximately saturated when V was 250 volts, but continued to increase slightly up to the highest potentials used.

Fig. 2.
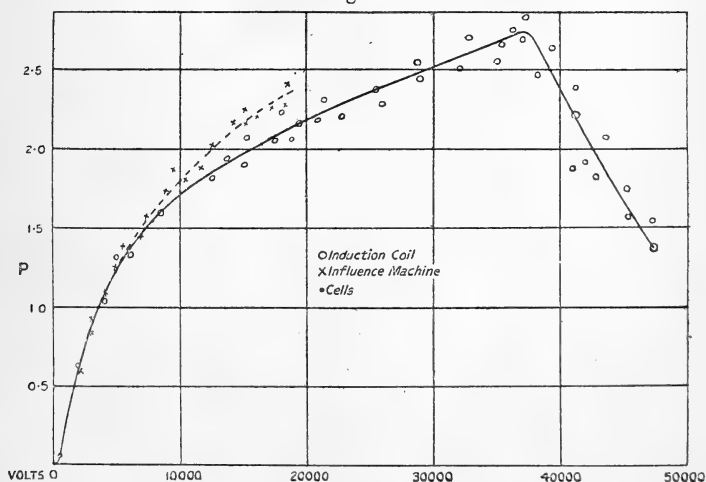
6. The results obtained are shown in figs. 2, 3, 4. Figs. 2 and 3 give the results for P, fig. 4 those for R.

3 E 2

Fig. 3 merely shows the part of the curve for small values
of V on a scale larger than that of fig. 2. The continuous
and dotted curves in fig. 2 (and the marks o and ×, for

Fig. 3.
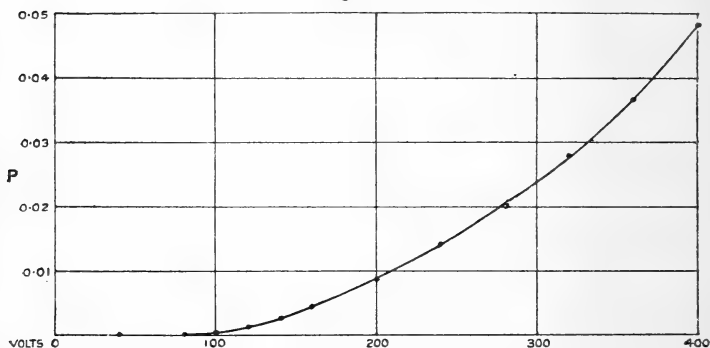
the corresponding observations) refer respectively to the
results obtained with the induction-coil and the influence-
machine. Not all the observations are plotted, but those
which are given are thoroughly representative.

Fig. 4.
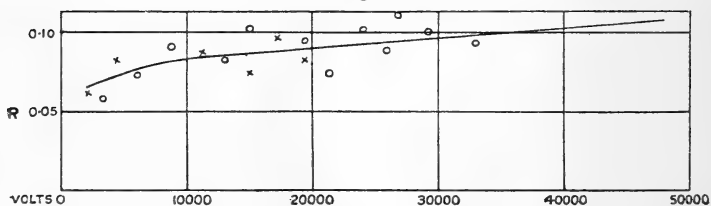
It will be observed that there is some difference between
the observations with the influence-machine and those with
the induction-coil, the values of P for the latter being some-
what lower. The difference cannot be due to the coil giving
a "reverse current," for the presence of such a current
would decrease i_1 and increase i_2 (since cathode rays also
cause ionization) and so increase P. I am inclined to think
that the smaller values of P with the coil are due to a lack
of homogeneity of the positive rays and the presence of some
possessing energies considerably lower than the maximum
indicated by the spark-gap, a conclusion which is enforced by
the fact that the results were much more regular and con-
sistent when the influence-machine was used. In an attempt
to extend the observations with the machine to higher values
of V, a serious accident to the apparatus occurred. Since the

observations must necessarily be interrupted for some time, and since it is proposed so to rearrange the apparatus that direct observation of the speed of the particles can be made by the use of a magnetic field, it appears better to give the results already attained than to wait for a complete elucidation of this matter which, I feel sure, will not affect the main conclusions.

A limit to the values of V which could be investigated was set by the occurrence of a discharge between S and A. If this discharge had been regular it would probably not have made measurements impossible ; but, as might be expected in so high a vacuum, the discharge appeared as a flickering green phosphorescence on the glass walls, while the current through the tube varied wildly. Work at higher potentials will probably be possible only if the continual evaporation of gas from the walls of the vessel is obviated by the methods employed in the making of X-ray bulbs. The highest reading of V for which any satisfactory reading was obtained was 54,000 volts (equivalent to a spark-gap of 2·7 cm.) ; the corresponding value of P was 0·5 ; it is not shown in fig. 2.

7. No very great interest attaches to the values of R plotted in fig. 4. The readings obtained are somewhat irregular, but it must be remembered that an error of 1 per cent. in i_1 or i_3 means an error not less than 10 per cent. in the value of R. The greatest value of R obtained was about 0·1, agreeing with the value assigned by Füchtbauer. R does not decrease very rapidly with the energy of the primary rays until that energy is less than 1000 volts. For $V = 400$ I could detect no difference between i_1 and i_3 ; R was certainly less than 0·01. When V was greater than 30,000 volts, the readings for i_1 became so irregular that no satisfactory values for R could be obtained ; but the curve has been extrapolated beyond this limit for reasons which will be noted immediately.

8. Fig. 3 shows that the curve for P approaches the axis of zero ionization asymptotically. There is, therefore, no definite ionization potential such as is found for cathode rays. This conclusion agrees with that of v. Bahr and Franck for the ionization of a gas ; but while they find an appreciable ionization of a gas for potentials as low as 10 volts, I have been unable to detect any sign of ionization below 40 volts. For 80 volts P is about 0·0005 ; for 40 volts it is certainly less than 0·0001. The difference in this respect between a metal and a gas may be due only to the possibility of detecting smaller ionization in the case of

the latter : the authors quoted do not state the lowest value for the ionizing power which they were able to detect. It was probably lower than that which could be detected in these experiments, but it is impossible to say whether this difference is sufficient to account for the difference in the limits of appreciable ionization.

9. The main interest of the experimental results lies in fig. 2, which shows that the ionization increases to a maximum at about 38,000 volts, and thereafter falls rapidly. This conclusion is so surprising that something should be said about the reliability of the measurements. There are three possible sources of error.

(1) The measurements made with the largest values of V were generally somewhat irregular and some of them were rejected altogether. The measuring apparatus was shielded effectively from the effects of the induction-coil ; but as soon as B or C was connected to it, the electrometer fluctuated, even when S was not heated and there was no appearance of a discharge from S to A. This effect may have been due to electrostatic induction through the tube opening into B, or, more probably, to charges creeping along the inner surface of the glass vessel with which A, B, and D were in contact only at a few points. The measurements of i_1, when B and D were connected to the measuring apparatus, were much more irregular than those when only C was so connected ; indeed, measurements of i_1 were practically impossible when V was greater than 35,000 volts. Though this difficulty was troublesome, there is no reason to believe that it had any effect but to make the observations vary somewhat widely about the true mean. All the measurements which in other respects seemed at all reliable agreed in showing a decrease in P for the highest values of the V.

(2) It is uncertain that the energy of the rays falling on C is actually that corresponding to the potential indicated by the spark-gap. There appears to be no method of removing this source of uncertainty other than measurements in a magnetic field which will permit the velocity of the rays to be found. Such measurements are about to be undertaken. But it is to be noted that the decrease in P will not be wholly illusory unless the average energy of the rays decreases notably as the equivalent spark-gap increases.

(3) It has been mentioned that at the highest values of V, i_1 could not be measured. The values of P plotted are those

given by

$$P = \frac{i_2 - i_3}{i_3} \cdot (1 - R),$$

$$= \frac{i_2 - i_3}{i_1},$$

i_2 and i_3 being measured while the values of R were taken from the extrapolated part of fig. 4. This procedure doubtless appears rash ; but it must be remembered that, if the real values of R are greater than the assumed, the real decrease in P will be more and not less marked than that shown. If, on the other hand (and it will be noted presently that this alternative is more probable), the real values of R are less, then, since R cannot be < 0, the values of P given will be at most 10 per cent. too small. It is impossible by any assumption concerning R to explain away the apparent decrease of P after the maximum. It may be added that any serious error on this account is highly improbable, for the measured values of i_3 were constant, so far as could be detected, for all values of V greater than 20,000 volts so long as the conditions of S (temperature and so on) were maintained constant. The decrease in P shown in the curve was due to a decrease in i_2, not to a change in i_3, and must therefore be attributed to a change in the electronic current from C.

10. Assuming that the form of the curve relating P and V is in the main correct, I think that we can obtain some idea of its significance by the light of a very interesting suggestion due to Ramsauer *. Noting that the velocity at which α-rays have their maximum ionizing power is nearly the same as the velocity at which electrons have their maximum ionizing power (about 10^9 cm./sec.), Ramsauer suggests that the ionizing power of a charged particle is a function of its velocity rather than of its energy, so long as this velocity is above a certain value. He shows that the form of the Bragg ionization curve for α-rays can be deduced with considerable accuracy by assuming that the ionization of α-rays of a given velocity is always proportional to (about 10 times greater than) the ionizing power of electrons of the same velocity. The limiting velocity, at which this relation ceases to hold, is the velocity of an electron (about 2×10^8 cm./sec.) corresponding to its ionization potential (11 volts in hydrogen) : particles which have less than this velocity, whether they be electrons or atoms, cannot penetrate within the atom, and the ionization (if any) which they produce is

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* K. Ramsauer, *Jahr. d. Rad. u. Elek.* ix. p. 515 (1912).

determined by actions quite different from that which results in the ejection of an electron from an atom into which the ionizing particle penetrates.

Now the experiments which have been described do not confirm completely Ramsauer's suggestion. Garratt * has shown that of the positive particles emitted from a heated phosphate some 10 per cent. are hydrogen atoms singly charged. According to Ramsauer, such particles ought to begin to display the high penetration and high ionizing power of α-rays when their velocity is that of 11-volt electrons ; such a velocity they would attain by falling through about 20,000 volts. Assuming, then, that Garratt's conclusion applies to the conditions of these experiments, there ought to have been found, according to Ramsauer, a rapid increase in the value of P for values of V greater than 20,000. No such increase was found, and so far the more advanced developments of Ramsauer's theory are rendered doubtful.

On the other hand we may, perhaps, express the fundamental idea of Ramsauer's theory in the following way :— The great difference in penetrating power and in ionizing power between α-rays and canal-rays is physically similar to the great difference in the same respects between electrons of which the energy is and of which the energy is not greater than 11 volts. In both cases he supposes the difference to arise from a difference in the power to penetrate the atom. Now in my experiments it is clear that the values of V (if there are such) for which the positive particles investigated become α-rays have not been reached ; accordingly it is to be expected that the relation between P and V should resemble the relation between these quantities for electrons of which the energy is less than 11 volts rather than that of electrons of which the energy is greater than 11 volts.

This expectation is fulfilled. From v. Baeyer's work † we know that as the energy of cathode rays falling on a metal plate is increased from 0, the number of electrons leaving the plate increases to a maximum at 5 volts and then falls to a sharp minimum just before 11 volts, where the rapid rise begins.

It is generally believed (for reasons which seem perfectly adequate) that these electrons leaving the plate when the energy of the incident cathode rays is less than 11 volts represent, not an ionization of the plate, but a reflexion of the incident rays. Nevertheless it is possible that the

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* A. E. Garratt, Phil. Mag. xx. p. 573 (1910).
† O. v. Baeyer, *Phys. Zeit.* x. p. 176 (1909).

analogy between the maximum with cathode rays at 5 volts followed by a fall, and the maximum with positive rays at 38,000 volts also followed by a fall, is not wholly false. The cause of both falls may be the same, namely the beginning of the stage at which the rays penetrate the surface of the plate.

11. It is suggested then that the fall of P for values of V greater than 38,000 volts represents the beginning of the stage at which the positive rays acquire one of the properties of α-rays—the power of penetrating atoms. And if this be so, we should expect that it would be followed shortly by the acquirement by the rays of the other property of α-rays, a great ionizing power ; we should expect that P after falling to a minimum should increase rapidly to a value characteristic of α-rays, and the form of the curve suggests, perhaps, that this rise should occur for some value of V less than 100,000 volts. It may, then, be possibly capable of observation.

If this view is correct, we should expect R as well as P to decrease after the maximum of P is attained. Unfortunately, as has been said, no evidence on this point is available. It is not to be expected that a similar fall in ionizing power would be found if the observations were made in a gas in which the rays are completely absorbed. For if, in the process of absorption in a gas, the speed of the rays is reduced to zero, it is almost impossible that faster rays should possess a smaller *total* ionizing power than slower rays : they could only possess (as in the case of α-rays) a smaller ionizing power over some portion of their range.

It remains to consider whether the view suggested is supported or refuted by any known facts. A definite penetration of atoms by the positive particles of canal-rays does not seem to have been observed. Goldsmith * has described observations which appear to show that such particles can make their ways through sheets of mica about 0·005 mm. thick, even when their energy is as low as 10,000 volts. But, since he could find no trace of *rays* after penetration, even when the initial energy was 35,000 volts, it is probable that such particles make their way between the atoms rather than penetrate through them, as do α-rays. On this side, then, there is no evidence that their penetration does not begin at about 38,000 volts.

On the other side, it is almost impossible to fix the least energy which confers on particles the properties of an α-ray. The least velocity of such rays which has been measured is

* A. N. Goldsmith, Phys. Rev. ii. p. 16 (1913).

about 5×10^8 cm. sec., corresponding to an energy (for a single electronic charge) of 5×10^5 volts; such rays are about 3 mm. from the end of their range in air. Their energy when they cease to penetrate must be considerably less, for it falls rapidly towards the end of their range, but no definite limit can be assigned. Moreover, it is clearly rash to assume too great a similarity between the properties of doubly charged helium atoms and singly charged hydrogen atoms. But at least nothing is known inconsistent with the view that the first stages of the conversion of canal-rays to α-rays begins at about 38,000 volts and is not complete at 50,000 volts. It is hoped that more light may be thrown on the matter by an improved apparatus in which higher values of V can be investigated (it does not seem impossible that 10^5 volts might be attained), the reliability of the measurements somewhat increased, and more information as to the nature of the particles obtained by deflecting them in a magnetic field.

12. In conclusion a numerical coincidence may be noted which is probably without theoretical significance. The maximum value of the ionization per incident particle observed in these experiments is within 10 per cent. the same as the maximum value observed with cathode rays, namely that at about 280 volts energy. The copper plate was throughout in the " state A " described in a recent paper *.

Summary.

The liberation of electrons from the surface of a copper plate struck by the positive particles from heated phosphates has been studied.

Figs. 2 and 3 give the relation between P, the number of electrons liberated by each positive particle, and V, the P.D. through which the particles have fallen.

Fig. 4 gives the relation between V and R, the reflexion-coefficient of the positive rays.

The significance of the results shown in fig. 2 is discussed. It is suggested that the fall in P for the largest values of V may be due to the beginning of the stage at which the particles can penetrate the surface-layer of the metal, exhibiting one of the properties which distinguish α-rays from canal-rays. At the highest potentials which could be studied no indication was obtained of the acquirement by the positive particles of the other distinctive property of α-rays, the great ionizing power.

Leeds, March 1915.

* N. Campbell, Phil. Mag. xxix. p. 369 (1915).

LXXXIII. *The Quantum-Theory of Radiation and Line Spectra.* By WILLIAM WILSON, *Ph.D., University of London, King's College* *.

IN his able report on Radiation and the Quantum-Theory Prof. Jeans †, dealing with theories of line spectra, remarks that Bohr's assumption is "not inconsistent with the quantum-theory and is closely related to it." The possibility therefore of deducing the results of Planck and Bohr from a single form of quantum-theory naturally suggests itself. Such a theory is developed in the present paper, and it will be seen that it contains that of Planck (in one of its forms) as a special case and, while formally distinct from Bohr's theory, leads to the same results when applied to the Rutherford type of atom in which an electron travels in a circular orbit round a positively charged nucleus.

This theory is based on the following hypotheses :—

(1) Interchanges of energy between dynamical systems and the æther, or between one dynamical system and another, are "catastrophic" or discontinuous in character. That is to say, each system behaves as a conservative one during certain intervals, and between these intervals are relatively very short ones during which definite amounts of energy may be emitted or absorbed.

(2) The motion of a system in the intervals between such discontinuous energy exchanges is determined by Hamiltonian dynamics as applied to conservative systems. It will be convenient to speak of a system, during such an interval, as being in one of its steady states.

(3) Let q_1, q_2, .. p_1, p_2, ... be the Hamiltonian positional and impulse coordinates of a system in one of its steady states, and let L be its kinetic energy, expressed as a function of $\dot{q}_1$, $\dot{q}_2$, ... and q_1, q_2, ... This function is homogeneous and of the second degree in $\dot{q}_1$, $\dot{q}_2$, ... If L contains products $\dot{q}_r \dot{q}_s$ $(r \neq s)$, we shall suppose them to have been removed by a substitution of the form :

$$\dot{q}_r = \alpha_{1r} \dot{q}_1' + \alpha_{2r} \dot{q}_2' + \ldots + \alpha_{nr} \dot{q}_n',$$

and we have therefore

$$L = \tfrac{1}{2}A_1\dot{q}_1^2 + \tfrac{1}{2}A_2\dot{q}_2^2 + \ldots + \tfrac{1}{2}A_n\dot{q}_n^2,$$

* Communicated by Prof. J. W. Nicholson.

† J. H. Jeans, Phys. Soc. Report on Radiation and the Quantum-Theory, p. 51 (1914).

and further

$$2L = \dot{q}_1 \frac{\partial L}{\partial \dot{q}_1} + \dot{q}_2 \frac{\partial L}{\partial \dot{q}_2} + \dots + \dot{q}_n \frac{\partial L}{\partial \dot{q}_n},$$

and consequently

$$
\left.
\begin{aligned}
2L_1 &= \dot{q}_1 p_1 \\
2L_2 &= \dot{q}_2 p_2 \\
&\cdots\cdots \\
2L_n &= \dot{q}_n p_n
\end{aligned}
\right\} \qquad \dots \quad \dots \quad (1)
$$

where $\qquad L_1 = \frac{1}{2} A_1 \dot{q}_1{}^2, \quad L_2 = \frac{1}{2} A_2 \dot{q}_2{}^2,$ &c.

We assume that the system in one of its steady states has a period $\frac{1}{\nu_1}$ corresponding to $\dot{q}_1$, $\frac{1}{\nu_2}$ corresponding to $\dot{q}_2$, and so on. From the equations (1) we get

$$2 \int L_1 dt = \int p_1 dq_1$$

and similar equations containing L_2, L_3, &c. Our third hypothesis can now be stated as follows :—The discontinuous energy exchanges always occur in such a way that the steady motions satisfy the equations:

$$
\left.
\begin{aligned}
\int p_1 dq_1 &= \rho h \\
\int p_2 dq_2 &= \sigma h \\
\int p_3 dq_3 &= \tau h \\
&\cdots\cdots\cdots
\end{aligned}
\right\} \qquad \dots \quad \dots \quad (2)
$$

where ρ, σ, τ, ... are positive integers (including zero) and the integrations are extended over the values p_s and q_s corresponding to the period $\frac{1}{\nu_s}$. The factor h is Planck's universal constant. It will be convenient to denote these integrals by H_1, H_2, ... respectively.

We shall now consider the statistical equilibrium of a collection of N similar systems of the type specified above. Let $N_{\rho\sigma\tau}$ ... be the number of systems for which $H_1 = \rho h$, $H_2 = \sigma h$, $H_3 = \tau h$, and so on ; and $N_{\rho'\sigma'\tau'}$ ... the number of systems for which $H_1 = \rho' h$, $H_2 = \sigma' h$, $H_3 = \tau' h$ .... Let us further write

$$f_{\rho\sigma\tau} \dots = \frac{N_{\rho\sigma\tau} \dots}{N} \qquad \dots \quad \dots \quad (3)$$

so that we have

$$\sum_{\rho=0}^{\rho=\infty} \sum_{\sigma=0}^{\sigma=\infty} \sum_{\tau=0}^{\tau=\infty} \ldots f_{\rho\sigma\tau}\ldots = 1. \quad \ldots \quad (4)$$

For the sake of brevity we shall say that $N_{\rho\sigma\tau}\ldots$ systems are on the locus $(\rho\sigma\tau \ldots)$, $N_{\rho'\sigma'\tau'}\ldots$ on the locus $(\rho'\sigma'\tau' \ldots)$, and so on. We have for the energy of the whole collection of systems the following expression:—

$$E = N \sum_{\rho=0}^{\rho=\infty} \sum_{\sigma=0}^{\sigma=\infty} \sum_{\tau=0}^{\tau=\infty} \ldots E_{\rho\sigma\tau}\ldots f_{\rho\sigma\tau}\ldots \quad . \quad (5)$$

where $E_{\rho\sigma\tau}\ldots$ is the energy of a system on the locus $(\rho\sigma\tau \ldots)$. If P is the number of ways in which N systems can be distributed, so that $N_{\rho\sigma\tau}\ldots$ lie on the locus $(\rho\sigma\tau \ldots)$, $N_{\rho'\sigma'\tau'}\ldots$ on the locus $(\rho'\sigma'\tau' \ldots)$, and so on, we have

$$P = \frac{N\,!}{(N_{\rho\sigma\tau}\ldots)\,!\ (N_{\rho'\sigma'\tau'}\ldots)\,!\ \ldots} \quad \ldots \quad (6)$$

We shall call P (after Planck) the "thermodynamic probability" of the distribution in question, and identify the quantity

$$\phi = k \log P \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

with the *entropy* of the assemblage of systems; the quantity k is the entropy constant. We may assume $N_{\rho\sigma\tau}\ldots$, $N_{\rho'\sigma'\tau'}\ldots$, and *a fortiori* N to be individually very large numbers, and therefore, by Stirling's theorem,

$$P = \frac{N^N}{\left(N_{\rho\sigma\tau\,\ldots}^{N_{\rho\sigma\tau}\,\ldots}\right)\left(N_{\rho'\sigma'\tau'\,\ldots}^{N_{\rho'\sigma'\tau'}\,\ldots}\right)\ldots}$$

This last equation, together with (3) and (7), leads to the following expression for the entropy of the collection of systems :—

$$\phi = -kN \sum_0^\infty \sum_0^\infty \sum_0^\infty \ldots f_{\rho\sigma\tau}\ldots \log f_{\rho\sigma\tau}\ldots \quad . \quad . \quad (8)$$

The condition for statistical equilibrium is expressed by

$$\delta\phi = 0,$$

where the variation is subject to the total energy being

constant, and also to equation (4). We easily obtain, by the usual variational method,

$$1 + \log f_{\rho\sigma\tau}\ldots + \beta\mathrm{E}_{\rho\sigma\tau}\ldots + \gamma = 0$$

$$\text{or}\quad f_{\rho\sigma\tau}\ldots = \mathrm{A}e^{-\beta\mathrm{E}_{\rho\sigma\tau}\ldots} \quad . \quad . \quad . \quad . \quad (9)$$

The value of A is determined by equation (4). The quantity β can be shown to be equal to $\dfrac{1}{k\mathrm{T}}$, where T is the absolute temperature of the collection of systems. From (8) and (9) we find

$$\phi = -k\mathrm{N} \sum_0^\infty \sum_0^\infty \sum_0^\infty \ldots \mathrm{A}e^{-\beta\mathrm{E}_{\rho\sigma\tau}\ldots}(\log \mathrm{A} - \beta\mathrm{E}_{\rho\sigma\tau}\ldots)$$

$$\text{or}\quad \phi = -k\mathrm{N}\log\mathrm{A} + k\beta\mathrm{N}\sum_0^\infty\sum_0^\infty\sum_0^\infty\ldots\mathrm{A}\mathrm{E}_{\rho\sigma\tau}\ldots e^{-\beta\mathrm{E}_{\rho\sigma\tau}\ldots},$$

and therefore by (5) and (9)

$$\phi = -k\mathrm{N}\log\mathrm{A} + k\beta\mathrm{E}. \quad . \quad . \quad . \quad (10)$$

On differentiating with respect to β we get

$$\frac{d\phi}{d\beta} = -k\mathrm{N}\frac{d\log\mathrm{A}}{d\beta} + k\mathrm{E} + k\beta\frac{d\mathrm{E}}{d\beta}, \quad . \quad . \quad (11)$$

and since

$$1 = \mathrm{A}\sum_0^\infty\sum_0^\infty\sum_0^\infty\ldots e^{-\beta\mathrm{E}_{\rho\sigma\tau}\ldots}$$

we have

$$0 = \frac{d\mathrm{A}}{d\beta}\cdot\frac{1}{\mathrm{A}} - \mathrm{A}\sum_0^\infty\sum_0^\infty\sum_0^\infty\ldots\mathrm{E}_{\rho\sigma\tau}\ldots e^{-\beta\mathrm{E}_{\rho\sigma\tau}\ldots}$$

$$\text{or}\qquad\qquad \frac{d\log\mathrm{A}}{d\beta} = \frac{\mathrm{E}}{\mathrm{N}}.$$

Substituting this in equation (11) we see that

$$\frac{d\phi}{d\beta} = k\beta\frac{d\mathrm{E}}{d\beta}$$

$$\text{or}\qquad\qquad \frac{d\phi}{d\mathrm{E}} = k\beta.$$

Therefore $k\beta = \dfrac{1}{\mathrm{T}}$. The law of distribution of the systems

among the different loci is therefore expressed by

$$f_{\rho\sigma\tau\ldots} = \frac{e^{-\frac{E_{\rho\sigma\tau\ldots}}{kT}}}{\sum_{0}^{\infty}\sum_{0}^{\infty}\sum_{0}^{\infty}\ldots e^{-\frac{E_{\rho\sigma\tau\ldots}}{kT}}} \quad \cdots \quad (12)$$

when equilibrium has been attained.

Equations (5) and (12) give us, for the average energy of a system,

$$\overline{E} = \frac{\sum_{0}^{\infty}\sum_{0}^{\infty}\sum_{0}^{\infty}\ldots E_{\rho\sigma\tau}\ldots e^{-\frac{E_{0\sigma\tau\ldots}}{kT}}}{\sum_{0}^{\infty}\sum_{0}^{\infty}\sum_{0}^{\infty}\ldots e^{-\frac{E_{\rho\sigma\tau\ldots}}{kT}}} \quad \cdots \quad (13)$$

Theory of Radiation.

The foregoing results are very general. We shall show that they include Planck's theory (one form of it at any rate) as a special case. We may write the equation of motion of one of Planck's oscillators, when in a steady state, in the form

$$m\frac{d^2q}{dt^2} + Kq = 0.$$

The most convenient form of solution for our purpose is

$$q = R\cos(2\pi\nu t - \theta), \quad \cdots \quad (14)$$

where R and θ are the constants of integration, and therefore

$$p = -2\pi\nu m R\sin(2\pi\nu t - \theta). \quad \cdots \quad (15)$$

The energy of such an oscillator is easily shown to be

$$2\pi^2\nu^2 m R^2. \quad \cdots \quad (16)$$

Now we have, from (14) and (15),

$$\int_{t}^{t+\frac{1}{\nu}} p\,dq = 4\pi^2\nu^2 m R^2 \int_{t}^{t+\frac{1}{\nu}} \sin^2(2\pi\nu t - \theta)\,dt,$$

and consequently

$$\rho h = 2\pi^2\nu m R^2,$$

and therefore, by (16),

$$E_\rho = \rho h\nu. \quad \cdots \quad (17)$$

On substituting this value of E_ρ in (12) we find that

$$f_\rho = \left(1 - e^{-\frac{h\nu}{kT}}\right) e^{-\frac{\rho h\nu}{kT}} . \quad . \quad . \quad . \quad (18)$$

Therefore the law of distribution of the oscillators among the different loci is precisely that given by Planck [*].

From (13) and (17) we deduce for the average energy of an oscillator

$$\overline{E} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} , \quad . \quad . \quad . \quad . \quad . \quad (19)$$

a well known result in Planck's theory. It may therefore be said that the proposed theory includes that of Planck (at least in one of its forms).

We may regard the æther as a collection of oscillators which, through the medium of matter, exchange energy with one another. The number of these, per unit volume, in the frequency range between ν and $\nu + d\nu$, has been shown by Jeans and others [†] to be

$$\frac{8\pi\nu^2 d\nu}{c^3} ,$$

where c is the velocity of radiation in the æther. The most probable distribution of these oscillators among the loci mentioned above, *i. e.* the distribution corresponding to maximum entropy, is one which makes their average energy

$$\frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} ,$$

and therefore we get for the energy within the frequency range ν to $\nu + d\nu$,

$$U_\nu d\nu = \frac{8\pi h\nu^3}{c^3} \cdot \frac{d\nu}{e^{\frac{h\nu}{kT}} - 1} ,$$

which is Planck's radiation formula.

Theory of Line Spectra.

We shall now show that Bohr's [‡] assumptions, in so far at any rate as we restrict ourselves to the type of atom or

* M. Planck, 'Theorie d. Wärmestrahlung,' p. 139, equations (220) and (227), second edition.
† J. H. Jeans, Phil. Mag. x. p. 91 (1905) ; M. Planck, *loc. cit.* p. 175.
‡ N. Bohr, Phil. Mag. xxvi. p. 1 (1913).

emitting system to which Bohr's theory has been applied with some measure of success, can be immediately deduced from the theory outlined above. The systems which he assumes to emit the hydrogen, helium, and other spectra are characterized, in their steady states, by constant kinetic energy, and by one positional coordinate q. The hypothesis expressed by equations (2) takes, for such systems, the form

$$2L \int_{t}^{t+\frac{1}{\nu}} dt = \rho h$$

or
$$L = \frac{\rho h \nu}{2}, \quad \ldots \ldots \quad (20)$$

and, since L in these systems is numerically the same as Bohr's* W, we see that (20) expresses Bohr's principal hypothesis. A further assumption made by Bohr is that the energy emitted by an atom, in passing from one steady state to another, is exactly equal to $h\nu_1$, where ν_1 is the frequency of the emitted radiation. Now according to the foregoing theory, since the energy of the æther vibrations of frequency ν must be equal to $rh\nu$ (equation (17)), where r is a positive integer or zero, it follows that the energy emitted by an atom (like those assumed by Bohr) must be equated to

$$r_1 h\nu_1 + r_2 h\nu_2 + \ldots, \quad \ldots \ldots \quad (21)$$

where the r's are integers, not necessarily all positive, and $\nu_1, \nu_2 \ldots$ are the frequencies of the corresponding æther vibrations. The present theory therefore includes this second assumption of Bohr's as a special case.

The conclusion that energy emissions to the æther are represented by an expression of the form (21), and are not necessarily monochromatic in all cases, receives some support from Prof. Barkla's experimental work on X-radiation †. It is noteworthy that Barkla finds that the energy absorbed from the primary radiation, during the production of the "fluorescent" radiations, is equal to

$$\tfrac{1}{2}mv^2 + h\nu_K + h\nu_L$$

per electron emitted, the first term representing the kinetic energy of the emitted electron and ν_K, ν_L the frequencies of the "fluorescent" radiations.

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* N. Bohr, *loc. cit.*
† C. G. Barkla, 'Nature,' 4th Mar. 1915.

The main object of this paper is to show that the form of quantum-theory which seems necessary to account for line spectra is not really distinct from that originally proposed by Planck, and the subject of its further application to line spectra and other phenomena may be left for a future publication.

In conclusion I wish to express my thanks to Professors J. W. Nicholson and O. W. Richardson for their advice and criticisms.

Wheatstone Laboratory, King's College,
          March 1915.

LXXXIV. *Negative Thermionic Currents from Tungsten. By* K. K. Smith, *A.B., Fellow in Physics, Princeton University* *.

Introduction.

THE emission of negative electricity from an incandescent metal or carbon filament has been the subject of several investigations †. The number of electrons carried from the filament to a neighbouring positively charged electrode increases very rapidly with the temperature. The exact quantitative relation between the number of electrons emitted and the temperature of the filament was established by Richardson, and has been verified by the experiments of others. It was assumed that the emission is determined simply by the number of electrons whose kinetic energy is sufficient to overcome the forces tending to prevent their escape from the metal.

This relation is expressed by the formula

$$i = a\mathrm{T}^{\frac{1}{2}}e^{-\frac{b}{\mathrm{T}}},$$

where i is the saturation (maximum) current in amperes per square cm. and T is the absolute temperature. The quantities a and b are constants, the latter being proportional to the work done by an electron in escaping from the metallic surface. On this view, a pure metal in a perfect vacuum would give a thermionic current which would be a function of its physical properties only. In any actual case the presence of traces of impurities or gases would presumably

have secondary effects, but would not be required to explain the existence of the current.

In view of some recent experiments *, which seemed to cast doubt upon the above explanation of thermionic currents, the following investigation was undertaken. Professor Richardson has already published the results of the earlier experiments †. The object has been (1) to make a detailed quantitative investigation of the negative thermionic emission from tungsten over a large temperature range, and (2) to discover, if possible, more evidence as to the conditions which determine the emission.

Experimental Arrangements.

The filaments used in these experiments were all taken from a spool of pure ductile tungsten furnished by the General Electric Co., Schenectady, N.Y. They were 0·041 mm. in diameter, and the lengths used in the different lamps varied from 2·5 cm. to about 9 cm. They were electrically welded in hydrogen to copper leads, which, in turn, were welded to platinum wires. Then the wires were mounted axially in cylindrical glass tubes and sealed in. The tubes were 3·2 cm. in diameter, and contained copper gauze cylinders 2·6 cm. in diameter. Separate wires connected these anodes to the outside of the lamps.

Fig. 1.
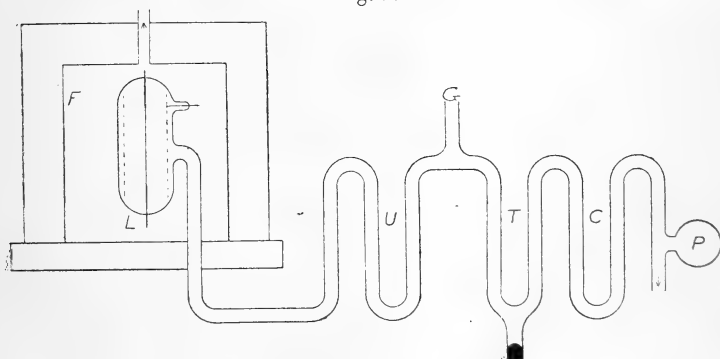
Fig. 1 shows the arrangement for exhausting and heating the lamp L, in the vacuum furnace. The figure is purely diagrammatic and is not drawn to scale. The U-tube, U,

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* Pring and Parker, Phil. Mag. vol. xxiii. p. 192 (1912); Pring, Proc. Roy. Soc. London (A), vol. lxxxix. p. 344 (1913); Fredenhagen, *Deutsch. Phys. Gesell. Verh.* vol. xiv. p. 384 (1912).

† Richardson, Phil. Mag. vol. xxvi. p. 345 (1913).

could be surrounded with a Dewar flask containing liquid air. The pressure indications were read on the McLeod gauge, G. By raising or lowering the mercury at T, the lamp and gauge could be shut off from the vacuum-pump, or connected to it. The tube C was half filled with coconut charcoal, and could be surrounded with liquid air when it was desired to reduce the pressure as much as possible. A bulb, P, containing phosphorus pentoxide, was attached between C and the Gaede mercury pump, and auxiliary pump. The furnace itself was evacuated by a separate pump.

The lamp was exhausted and heated at the same time. The furnace reached a maximum temperature of about 600° C., which was maintained for several hours in order to get rid of absorbed gases. At first considerable quantities of gas were given off, but the pressure gradually decreased with prolonged heating, and finally became quite small. The furnace was then allowed to cool slowly, liquid air was applied at U and C, and the filament was heated by an electric current. The cylinder was charged positively, so as to be bombarded by electrons from the filament. At intervals the amount of gas still being driven off was estimated by closing the trap T for five minutes, and noting the increase of pressure, if any. The details of some of these experiments, which have already been published *, show that the observed thermionic currents were too large to be ascribed to the evolution of gas from the filament, or to an action depending upon impacts between the gas molecules and the filament. After the pressure indicated on the gauge had become practically inappreciable, the lamp was either sealed off immediately and removed, or the observations were taken on the unsealed lamp.

Measurement of Currents.

The lamp filament was usually made one arm of a Wheatstone's bridge. The positive terminal of a battery was connected to the receiving electrode, and the other terminal to the positive end of the filament. An electrometer having a sensibility of 790 divisions per volt, and a capacity of 130 electrostatic units, was used to measure the smallest currents. A condenser whose capacity could be varied from 0·001 microfarad to 1 microfarad was used in parallel with the quadrants when necessary. With larger currents, resistances varying from 100 ohms to 1 megohm were put in the

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* Richardson, *loc. cit.*

thermionic circuit, and the quadrants were connected to the ends of these resistances in turn. For currents greater than 1 microampere a unipivot galvanometer with variable shunts was used. With these arrangements, it was possible to measure the emission over a range from 10^{-13} amp. up to 1 ampere. Owing to the high melting-point of tungsten, it was possible to obtain thermionic currents of the order of magnitude of the heating currents. In what follows, the thermionic current will usually be expressed in terms of unit area, otherwise it is to be taken as the total current from the filament.

Measurement of the Filament Temperatures.

Through the kindness of Dr. Irving Langmuir, a curve was obtained with the wire, showing the temperature of the filament as a function of the current carried by it. This curve was determined by photometric measurements on a special lamp, using a piece of the same wire that was used in these experiments. As a check on the temperature determinations some small lamps were made from these filaments, and were used in an optical pyrometer of the Holborn-Kurlbaum type, constructed in this laboratory. These lamps were calibrated by observations on a black-body furnace at the melting-points of copper and nickel. The results of the two methods were in satisfactory agreement. In the earlier experiments it was customary to determine the resistance each time an observation was taken, since the bridge galvanometer was of course much more sensitive than the ammeter to small variations in the temperature of the filament.

The effects produced by a thermionic current in the ordinary Wheatstone's bridge circuit have been considered by Richardson and Cooke *. As far as the present experiments are concerned these effects are of no importance, so long as the thermionic current is small in comparison with the heating current. For very high temperatures, however, the large thermionic currents cause the temperature estimations to be much too high. In fact, even if the bridge is not used at all, the temperature of the filament will be over-estimated if a large thermionic current is flowing, and, furthermore, the two ends will be unequally heated. For a given current per square centimetre these disturbing effects increase with the length of the filament.

* Phil. Mag. vol. xx. p. 173 (1910).

Experimental Results.

Lamp 1.

Lamp 1 contained a filament 5 cm. long, and a cylindrical anode. After the lamp had been heated in the furnace for 9 hours, liquid air was applied at U and C, and the filament was glowed for an hour and a half at various temperatures above 2500° K. The thermionic currents varied from 3 to 40 milliamperes. The trap T was closed at intervals, and the increase in pressure during five minutes was noted. In the first period the pressure rose from 0·005 to 0·050 micron : in the last period the increase was from " 0 " to 0·003 micron. The furnace (still above room temperature) was then opened, and the lamp was sealed immediately. The pressure indicated was " 0."

Professor Richardson measured five series of thermionic currents greater than 1 microampere, the potential difference between the anode and the cathode being 120 volts. The results are shown in fig. 2, in which $\log i - 1/2 \log T$ is plotted against 10000/T. Series 1 A, 2 A, and 3 A were taken with decreasing temperatures, the others with increasing temperatures. It will be noticed that the points for the 3rd series are shifted to the left of the preceding ones. At first sight, this would seem to indicate less current at a given temperature as the heating was continued. It is believed, however, that this is not to be ascribed primarily to a change in the emitting power of the surface, but rather to a change in the resistance of the filament, owing to excessive heating. After the first series of readings, the filament was heated for over an hour at a temperature above 2500° K. The thermionic current was turned off to prevent unequal heating, which is likely to burn the filament out at one end. Between the 2nd and 3rd series the filament was heated to a still higher temperature for 20 minutes, and the resistance increased from 1625 to 1670 units, or about 2·8 per cent. The same thermionic current was obtained with R = 960 after overheating as with R = 945 just before. These resistance changes as the filament evaporates cause the temperatures to be overestimated, and are sufficient to account for the above variations in thermionic current.

In series 4, thermionic currents (not shown in fig. 2) up to 320 milliamps. were obtained, or 8 times as much as had been obtained before the lamp was sealed off. Immediately after this large current was obtained, it was found that at

2480° K. the current was only 22·5 milliamps., whereas it had been 58 milliamps. just before this.   Series 5, taken

Fig. 2.
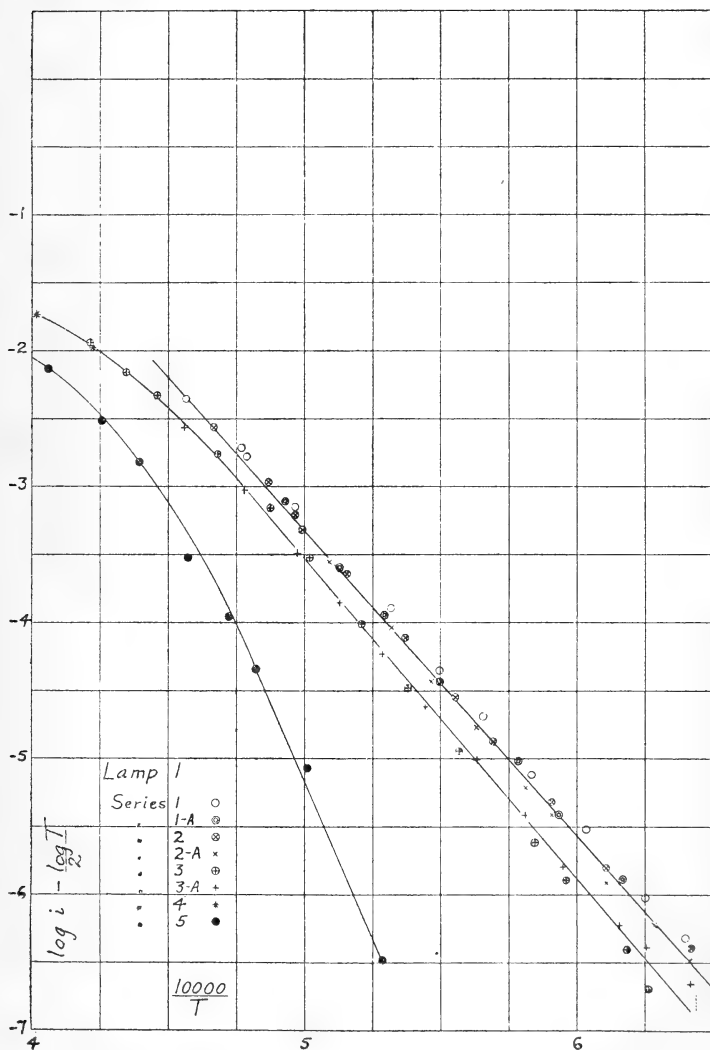
immediately afterwards, shows the effects of this severe heating in a more striking manner.   The filament was about

300° hotter than usual before the current was large enough
to be read on the microammeter. At this higher temperature,
1890° K., the current was now only 0·014 milliamp. per
sq. cm., as compared to 5·36 milliamp. per sq. cm. at the
same temperature in series 2. In other words, the thermionic
current had been reduced to 1/380th part of what it had
been. It began to increase very slowly, although the tempe-
rature was constant. The other points of series 5 were
determined at once, without waiting to see if the current
would become steady at the lower temperature. The current
increased with the temperature much more rapidly than
before, and approached the preceding series so that at the
highest temperature it was 60 per cent. of the current at
the same temperature in series 4. About 2500° K. a blue
glow appeared after continued heating, and the copper anode
became red-hot.

The above experiments were performed before Dr. Lang-
muir's paper * on thermionic currents was published. They
confirm his conclusion that the effect of residual gases is
to decrease the thermionic current, especially at low tempe-
ratures. The fact that considerably larger currents, at the
same temperatures, have been obtained by the writer is
undoubtedly owing to better vacuum conditions. According
to the above paper, the normal vacuum curve was obtained
at a pressure of 0·07 micron, and gives the following values :
$a = 34 \times 10^6$ amps. per sq. cm., $b = 55,500$. By the use of
charcoal and liquid air, as described before, it has been
possible to keep the pressure as low as 0·001 micron, or
less.

In Lamp 1, so long as the thermionic current did not
exceed those employed before the lamp was sealed, the
vacuum was practically perfect, and very large currents
were obtained. At 2000° K. 26 milliamperes per sq. cm.
were measured. Later, the excessive heating and bombard-
ment of the anode by electrons liberated occluded gas, which
reduced the thermionic current. The presence of gas is
proved by the blue glow which appeared. There is no
reason to suppose that any appreciable amount of gas was
present previous to the excessive heating. Tests have been
made at various times with an induction-coil, on similar
lamps which had not been overheated, and no indications of
gas were ever found. The potential difference and the size
and shape of the anode were such as to permit the normal

* Phys. Rev. ii. p. 450 (1913).

current to flow unlimited by any space charge effect [*]. This is proved by the fact that the currents were practically saturated at 120 volts. Even with a blue glow in the lamp, the points at the upper end of curve 5 fall far to the left of the straight line. Hence this deviation cannot be the result of a space charge effect, but is undoubtedly caused by the large thermionic currents, which were of the order of magnitude of the heating current [†].

Lamp 2.

Lamp 2 contained a filament 8·5 cm. in length, and a cylindrical anode of copper gauze. It was heated for 14 hours in all, and liquid air was applied at C, but not at U (at first). The filament was glowed for about $3\frac{1}{2}$ hours, the thermionic current during the last hour being 10 milliamperes. In the first 5 minute test with the trap T closed, the increase of pressure was from 0·001 to 0·050 micron ; in the last 30 minutes the increase, if any, was not more than 0·0001 micron from " 0." Liquid air was then applied to U to condense the mercury vapour, but no change in the thermionic current could be detected. The lamp was then sealed, and the thermionic currents were measured from 1050° K. up. The results (plotted in fig. 3) show that within the limits of experimental error, the equation

$$i = aT^{\frac{1}{2}}e^{-\frac{b}{T}}.$$

is satisfied throughout. (In all the figures the current is expressed in amperes per sq. cm.)

In order to determine how the thermionic current depended upon the voltage, tests were made at the following temperatures : 1070, 1335, 1465, 1590, 1710, and 1825° K. To reduce the results to the same scale, the current with 200 volts has been taken as the unit measure in each case, and

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[*] Langmuir, *loc. cit.*

[†] Since these experiments were completed, Dr. Dushman has published (Phys. Rev. iv. p. 121, 1914) the results of some experiments in which he observed the decrease in the thermionic current caused by bombardment of the anode. The temperatures were above 2000° K. and the maximum currents obtained appear to be about the same as those observed by Dr. Langmuir. The values of the currents given for the Coolidge X-ray tube (Phys. Rev. ii. p. 409, 1913) are larger, but not so large as the writer's.

Fig. 3.
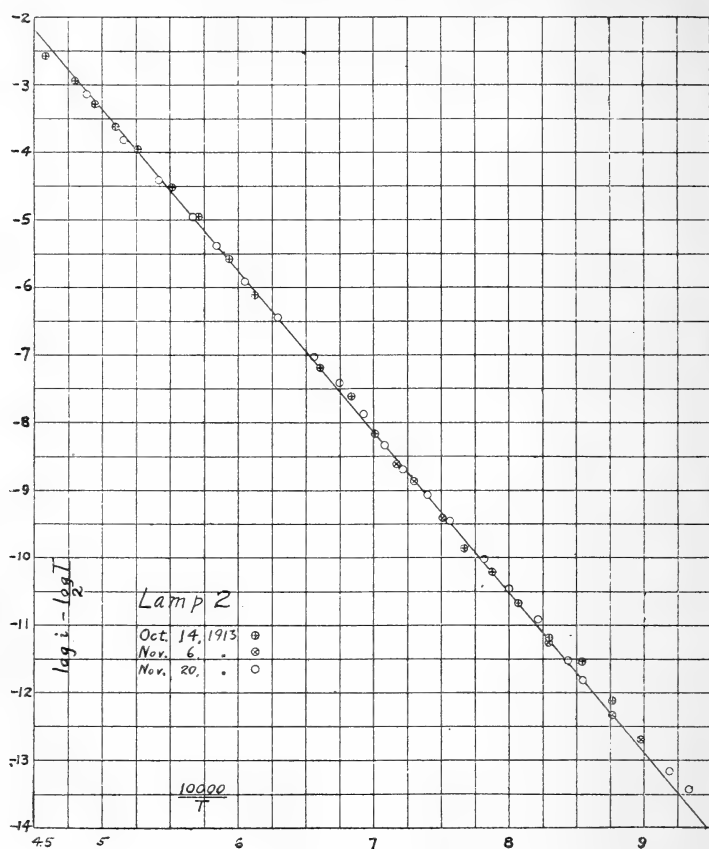
the ratios, which were the same for all the temperatures, are
shown in the following table:—

Volts.	Current. Current with 200 volts.
25	0·80
50	0·85
100	0·91
300	1·07
400	1·14
500	1·21
600	1·27

Table I. shows the values of the currents which best re-present the emission observed under good vacuum conditions in Lamps 1 and 2. They are given by the values :

$$a = 6\cdot7 \times 10^8 \text{ (amps. per sq. cm.)}, \quad b = 54700.$$

TABLE I.

Temperature.	Thermionic Current.
1050° K.	0·000000235 microamps.
1100	0·00000256 per
1150	0·0000227 sq. cm.
1200	0·000169
1250	0·00106
1300	0·00583
1350	0·0282
1400	0·122
1450	0·476
1500	1·70
1550	5·60
1600	17·1
1650	49·0
1700	132·
1750	337·
1800	809·
1850	1880·
1900	4120·
1950	8730·
2000	17800·
2050	35200·
2100	67000·
2150	124000·
2200	224000·
2250	394000·
2300	674000·

Lamp 3.

Lamp 3 contained a filament 5·25 cm. long and a copper gauze anode. It was given the usual treatment and sealed off, but the seal cracked while cooling. The apparatus was then arranged so that the thermionic currents could be measured with the lamp in place in the furnace, and connected to the McLeod gauge, etc. After the lamp had been re-heated and exhausted to a low pressure, the furnace was opened, liquid air was applied at U and C, and a series of observations was taken at once, beginning at low temperatures. The potential difference was 190 volts. At several points it was noticed that the current was unsteady, and that it increased with the time. In these cases, readings were taken every minute for 5 minutes or so, and the average reading was taken. The pressure was " 0 " at the beginning,

and did not exceed 0·002 micron until the current was as large as 0·130 amp. (1·95 amp. per sq. cm.). With this current the pressure increased (with the trap T closed) from 0·002 to 0·060 micron in 6 minutes. Currents as large as 0·350 amp. were observed, while the pressure increased to 0·600 micron, and then decreased to 0·400 micron. The temperature was at least 3000° K., and the filament burned out a few minutes later.

The results are shown in fig. 4. Points in the middle of the curve fall along a straight line from which the value $b = 69,500$ is calculated. At the lowest temperature (1950°) the current is about 1/600 of the current observed with Lamp 1 at the same temperature. At 2500° K. the corresponding ratio is about 1/3, while at the highest temperature the two currents are practically identical. These results will be discussed after they have been compared with those of the next experiment.

Lamp 4.

This lamp was an exact duplicate of the preceding one. After the usual treatment the filament was given its initial heating (by a current) at 2100° K. This was continued for $3\frac{1}{2}$ hours, during which time the thermionic current increased from 3 to 133 microamperes. The observations of the last 40 minutes are shown in the following table :—

Time.	Pressure.	Total Current.
10.42 P.M.	0·006 micron.	16
.45		18
.47		21·5
.50		27·5
.52		36·4
.53		42
.54		51
.55		66·5
.57	0·001	
.58		109
.59		114
11.00		116
11.20	0·0001	133

With a potential difference of 210 volts the 1st series of observations at different temperatures was taken, after which the thermionic circuit was broken, and the filament was glowed for 40 minutes at temperatures varying from 2700° to 3000° K. The 2nd and 3rd series were then taken in close succession. During all these series the pressure was " 0," according to the gauge, whether the trap T was closed

or not. This was true even after the filament was finally burnt out. All the observations are shown in fig. 4, for comparison with those of Lamp 3.

Fig. 4.
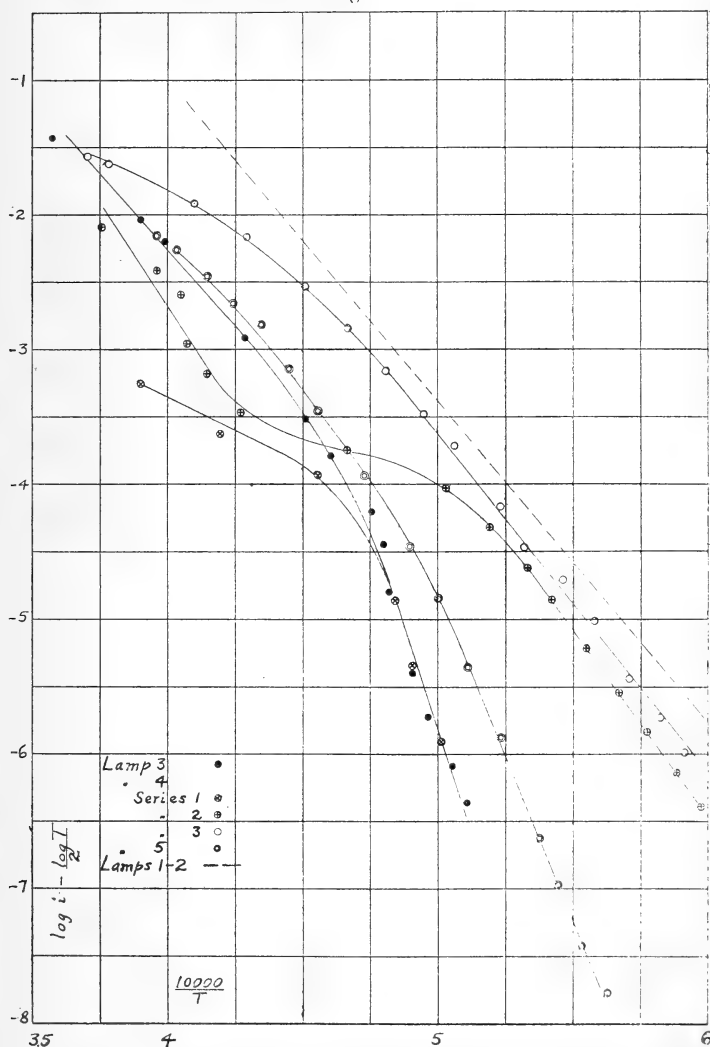
Taken together these two experiments show that the initial negative thermionic current is very much less than that obtained on subsequent heating. The actual difference would be more obvious if the currents, instead of their logarithms,

had been plotted. This conclusion was confirmed in every
·one of the subsequent experiments. Under some conditions,
as in the last experiment with Lamp 1, and in some others
to be described later, it is possible that the current may show
a decrease, but no emission less than the initial emission has
been observed.

The first observations on the two lamps (3 & 4) are in
good agreement at low temperatures, but at a certain point
the 1st series (Lamp 4) shows that the current is increasing
much more slowly with the temperature. The heating of
the filament at very high temperatures, with the thermionic
·circuit broken, was followed (series 2) by much larger
currents than before. At 2000° K. curve 2 bends sharply
to the left, and then again to the right, while curve 3 is
regular. Heating the filament would tend to remove im-
purities and absorbed gases from the filament. It is known,
for example, that the oxide volatilizes in a vacuum without
the evolution of gas. On the hypothesis that initially there
·existed a surface layer which hindered the emission of
·electrons, we should expect to find larger currents in the
second series. The falling off in the rate of increase with
the temperature, which occurred at about 2000° in the first
two series (Lamp 4), is caused by the bombardment of the
:anode. At low temperatures, and hence with smaller
·currents, the latter effect is not apparent. Heating the
filament to a high temperature without the thermionic
·current does not bombard the anode and free it from gas,
although it does rid the filament to a large extent of what-
ever is hindering the normal emission. Heating the filament,
and allowing the thermionic current to flow, cleans both
anode and cathode.

Lamp 5.

This lamp was like the preceding ones, except that the
filament was 6 cm. long. The observations were extended
over three days, and during this time there was always a
supply of liquid air about U and C. Out of ten series of
observations the largest currents are plotted in fig. 4. The
smallest currents were found when the filament was first
heated, and this agrees with the results of the other experi-
ments. With this lamp complete saturation was obtained,
whereas the results already given for Lamp 2 show that the
·currents always increased somewhat with the voltage. When
voltages as high as 600 volts were first applied the results
were as follows : at 1800° K. the current was saturated at
from 200 to 400 volts, and then decreased with increasing

voltage. The measurements were repeated immediately afterward, and it was found that the current had been reduced one half. At the same time the pressure had increased from 0·010 to 0·014 micron, owing, no doubt, to the evolution of gas from the anode.

The gas pressure, however, was evidently not an important factor in determining the thermionic current. For example, the same pressure (0·001 micron) was indicated in series 1 and 3, although the currents were considerably larger in the latter case. On the other hand, series 3, 8, and 9 agreed quite well, although the corresponding pressures were 0·001, 0·010, and 0·100 micron respectively. Repeated heating did not increase the emission beyond what is shown for this lamp in fig. 4. In view of these facts it was believed that the great reduction in current, as compared with the other lamps, must be caused by condensable vapour, probably water vapour. The lamp had been heated in the furnace to 500° C., or more, but there was the possibility that water vapour had entered afterwards from below the furnace, even though liquid air had been around the U-tube all the time. This was the first lamp which had not been sealed shortly after the furnace was opened. A slight change in the apparatus was therefore made before the next lamp was set up. The glass tube leading to the lamp was bent into a U inside the furnace, so that liquid air could be applied close to the lamp. Any vapour which might arise from the unheated tubing below the furnace would then be condensed before it could enter the lamp.

Lamp 6.

This lamp contained two parallel filaments, 1·7 cm. apart. One filament "A" was 8·5 cm. in length, and the other "B" 7·2 cm. It was then unnecessary to use a cylindrical gauze anode, and thus one possible source of gas was removed. All the platinum and copper connecting wires were completely covered with melted glass before they were sealed in the lamp, so that the only surfaces exposed on the inside of the lamp were of tungsten and glass. At the same time that the lamp was being heated in the furnace, the two filaments were glowed in series for six hours at temperatures varying between 2000 and 2500° K. As soon as possible after the hot furnace was opened, liquid air was placed around the new U-tube next to the lamp. Liquid air had previously been placed around the other U-tube and the charcoal tube as usual.

Using filament " A " as the hot cathode, three series of observations were made, and the results of the first and last are shown in Table II. Following the 2nd series, the cathode had been heated to 2700° K. for twenty minutes. After this the currents were as large, at the same temperatures, as the currents which had been observed in the sealed lamps. The pressure was " 0 " during the whole time. This experiment shows that the thermionic emission from tungsten is not a secondary effect arising from the presence of gas or condensable vapour, but must come from the metal itself.

TABLE II.

Current.		Temperature.		
(Amps. per sq. cm.)		" A," series 1.	" A," series 3.	" B," series 1.
$1·12 \times 10^{-5}$	....	1715° K.	1540	1695
2·25 ,,	....	1755	1575	1740
4·50 ,,	....	1795	1615	1785
9·0 ,,	....	1840	1650	1835
18·0 ,,	....	1895	1695	1890

Immediately after the 3rd series with filament " A " as cathode, filament " B " was made the cathode, and " A " the anode. The results of the first series of observations under these conditions are also shown in Table II. It will be seen that the emission under the same vacuum conditions depended upon which filament was used as the cathode. As stated above, both filaments had been glowed in series, and otherwise they had been treated alike, except that " A " had been heated to 2700° K. for twenty minutes. Above 1900° K. the currents were limited on account of the small dimensions of the anode, and after a certain value was reached the currents could not be increased, with constant voltage, no matter how much the temperature was raised.

The liquid air was then removed from the gauge and furnace U-tubes, the trap T being closed. The pressure increased from " 0 " to 0·25 micron, and the resistance of the glowing filament, " B," began to increase slowly. This was caused by the oxidation of the filament by the water vapour released from the U-tubes. The resulting ionization in the gas neutralized the space charge effect, and the current (T = 2180° K.) began to increase. Series 4, taken at once, showed that below 1950° K. the currents had been decreased

by the formation of the oxide, but above this temperature they were larger, for the reason just given. The following table shows how much the currents at 2040° were increased by the removal of the liquid air.

Volts.	Total Current in Microamperes.	
	Liquid Air on. P=0·0001 micron.	Liquid Air off. P=0·250 micron.
20	1·05	...
35	...	18
40	4·1	350
60	9·35	362
80	17·5	365
100	28·2	...
120	40·4	368

Below 2000° K. the currents were steady, but above this it was noticed that they increased with the time. The following table shows one instance of this, as well as the effect of replacing liquid air about the U-tube near the gauge.

Time.	Total Current (T=2010° K.).
0 mins.	350 microamperes.
1	368
1·5	375
2·0	388
3·0	410
3·5 P=0 220 micron.	
4·5	430
Liquid Air replaced.	
5 0	102
5·5	93
6·0	84
6·5	84
7·0 P=0·170	86
8·5	86
9	86
constant.	

The increase was probably caused by the more rapid removal of the oxide at this temperature, or to the increase in temperature due to the filament burning ; while the decrease was caused by the absence of ions after the condensation of

the water vapour. The resistance of the filament remained constant when liquid air was about the U-tube, otherwise it increased gradually. The liquid air was removed once more, and repeated measurements showed, as before, that the currents increased rapidly with the voltage when liquid air was around the U-tube ; if it was not, the currents were saturated. After the liquid air had once been removed the vacuum conditions were never so good as before, but the pressure was always so low (< 1 micron) that ionization by collision had no effect.

Lamp 7.

This experiment was undertaken in order to measure the currents before and after the lamp was sealed. The filament was 2·6 cm. long, and the anode was a cylinder of copper gauze. The lamp was heated 10 hours on one day, and 6 hours on the next day. After the first series of observations had been taken, the trap T was closed, and was kept closed until the lamp was sealed 6 hours later. The pressure was " 0 " before any measurements were taken, and no indication of pressure could be seen up to the time that the lamp was sealed. After sealing, the liquid air was removed from the U-tube, U, and three or four minutes later the pressure in the gauge was 0·370 micron, but it did not increase after that. This was the pressure of the gases that had been condensed.

The results of the typical series are shown in fig. 5. The first currents were less than those that had been observed in the first heating of the other filaments. Afterwards they increased, as can be seen in series 4. This condition was not permanent, however, for after the filament had been kept at a temperature of about 2000° K. for two hours, it was found that the currents were smaller than in series 4, although they were still much larger than in the 1st series. These results (series 6) have not been plotted, since they are represented well enough by series 9. After continued heating the emission was again about the same as in the 4th series, and the lamp was then sealed.

A few days later measurements were taken on the sealed lamp. Without any preliminary heating whatever, series 9 was taken with increasing temperatures, followed immediately by series 9 A with decreasing temperatures. It is evident that a marked change has been produced by simply heating the filament once. The final results have been plotted, and it will be seen that the points lie quite accurately

along a straight line through the whole range of tempera-
ture, which was from 1760° to 2520° K. The agreement

Fig. 5.
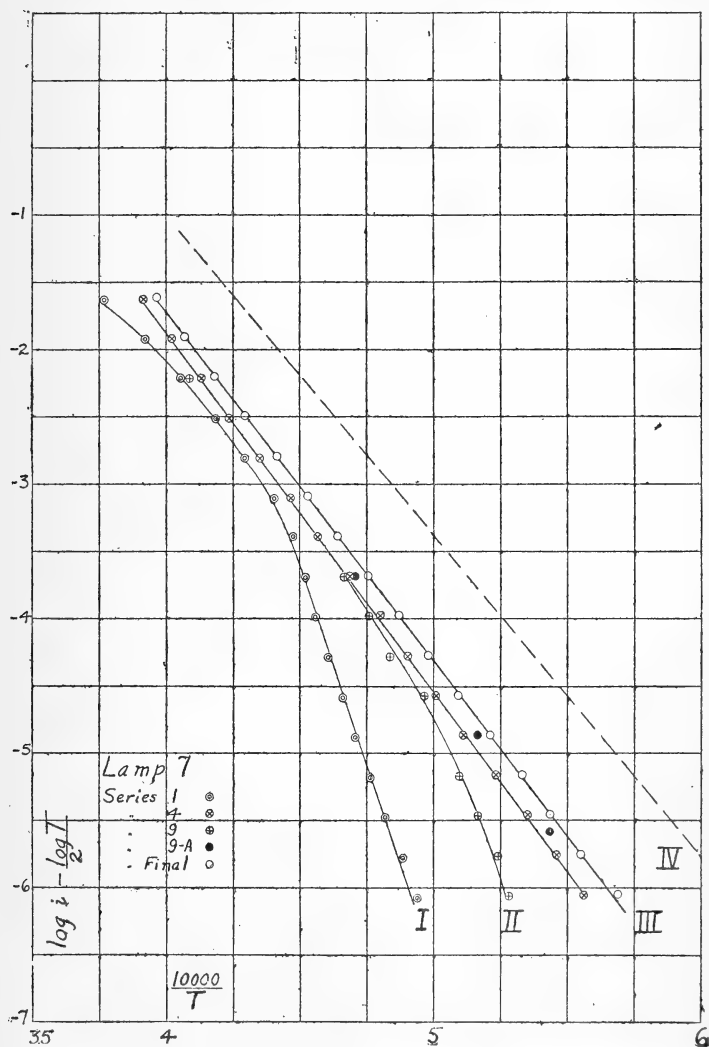
between the observed and calculated currents can be seen in
Table III.

The value of *b* (59700) is larger and the currents are

3 G 2

smaller for this lamp than for the other sealed lamps. The only known difference in treatment to which this can be ascribed is that this filament was never heated to a temperature so high as 2700° K., and to avoid the risk of burning out the filament, the temperature was seldom raised above 2500° K., except for short periods while observations were being taken. The close agreement indicated in Table III.

TABLE III.

Lamp 7.

T.	Current in microamperes per sq. cm.	
	Observed.	Calculated.
1760° K.	37·5	33·8
1800	75·0	78·0
1840	150·	157·
1875	300·	295·
1920	600·	607·
1965	1200·	1260·
2010	2400·	2460·
2050	4800·	4730·
2105	9600·	9680·
2155	19200·	19300·
2205	38400·	37800·
2265	76800·	76700·
2330	154000·	157000·
2390	308000·	311000·
2455	616000·	597000·
2520	1230000·	1190000·

$a = 4·4 \times 10^3$ amperes per sq. cm.
$b = 59700.$

does not, of course, prove that the emission was characteristic of the pure metal alone. An oxide, for example, could remain upon the wire indefinitely if the temperature were not raised too high. Four months after the lamp was sealed, experiments showed that the emission was unchanged. The filament was then heated to 2900° K. for three minutes, with a potential difference applied to prevent the thermionic current from flowing, but this produced little, if any, change in the emission at 1800° K. The temperature was then raised with the thermionic current flowing, but unfortunately the filament was burnt out near one end before any observations could be taken.

DISCUSSION OF RESULTS.

Figure 5 may also be used to illustrate the typical results of all the experiments. When the observations are plotted it is found that they fall into four groups, represented by curves I., II., III., IV., as follows :—

I. The first currents in four lamps (3, 4, 5, 7) (*cf.* also fig. 4). The first currents in the other lamps were not measured.

II. (*a*) The last series with lamp 1 (*cf.* fig. 2).
  (*b*) The currents after the liquid air was removed from lamp 6.
  (*c*) The largest currents in lamp 5 (*cf.* fig. 4).
  (*d*) The first currents after lamp 7 was sealed.

III. The permanent emission in lamp 7, which was not heated much above 2500° K. This would also include the currents from filament "B," lamp 6, before the liquid air was removed.

IV. The currents observed after heating the filaments to a very high temperature, 2700° K. or more, under the best vacuum conditions (lamps 1, 2, 6 "A").

These variations in the thermionic emission seem to be the results of progressive changes in the surface conditions [*]. When the filament is first heated its surface is probably slightly oxidized, and otherwise contaminated by impurities. No special precautions to clean the filament were taken before it was sealed in the lamp. After a good vacuum has been secured, heating the filament for a sufficient time to a temperature above 2700° K. removes the impurities, and then the emission is represented by IV. This condition is permanent thereafter provided the vacuum is maintained, but under the following circumstances the emission changes to II., which is not much larger than the original I. : (*a*) if gas is liberated inside the lamp by excessive heating and bombardment of the anode (lamp 1), or (*b*) if the filament is oxidized by allowing small amounts of water vapour to enter the lamp, as in 6.

The removal of impurities from the surface seems to be indicated quite clearly by the observations made when the filament in lamp 7 was first heated above 2000° K. after sealing. This changed the emission permanently from II. to III. Since the lamp had been sealed under good vacuum conditions there was no fresh supply of gas by which the

[*] *Cf.* Langmuir, *loc. cit.*

filament could again be contaminated. It should be recalled
that no emission greater than II. could be obtained in lamp 5,
and it seems quite likely that continued heating was futile
in this particular case, because the impurities were being
renewed as rapidly as they were driven off.

Barring lamp 3, which was burnt out at the end of the
first series, lamps 5 and 7 were the only ones in which the
currents represented by IV. were not obtained, and it seems
significant that these were the lamps which were not heated
much above 2500° K. Moreover, as already shown in
Table II., one filament in lamp 6 gave the large currents IV.,
but immediately afterwards, and under the same vacuum
conditions, the other gave currents approximately the same
as III. The former had been heated to 2700° K., whereas
the latter had not been heated above 2500° K. This is what
might be expected if the filaments contained an impurity
which could not be removed except at very high tempera-
tures. If the temperature were not raised too high the
impure surface would give continuously currents such as III.,
but after the impurity had been driven out, the permanent
thermionic emission, IV., would be characteristic of the pure
metal.

One of the most interesting results of these experiments
is the enormous range of validity established for the emission
formula

$$i = AT^{\frac{1}{2}}e^{-\frac{b}{T}},$$

when the conditions are such that no change in the character
of the emitting surface is believed to occur. The formula is
shown to hold good whilst the current is varied by a factor
of 10^{12}, the corresponding range of temperature being from
1050° K. to 2300° K. An equally good agreement is shown
with the formula $i = CT^2 e^{-d/T}$, with C and d constants and
d equal to 52000 ; so that it is not possible to distinguish
between the relative merits of these two formulæ with the
data so far obtained.

LXXXV. *Note on the Higher Derivative of a Function, the variable of which is a Function of an independent variable.* *By* I. J. SCHWATT *.

IN E. R. Hedrick's translation of Goursat's work 'A Course in Mathematical Analysis' appears the following problem (p. 32, 6.):—

Show that the nth derivative of a function $y = \phi(u)$, where u is a function of the independent variable x, may be written in the form

$$(a) \quad \frac{d^n y}{dx^n} = A_1 \phi'(u) + \frac{A_2}{1.2} \phi''(u) + \ldots + \frac{A_n}{1.2.3 \ldots n} \phi^n(u),$$

where

$$(b) \quad A_\kappa = \frac{d^n u^\kappa}{dx^n} - \frac{\kappa}{1} u \frac{d^n u^{\kappa-1}}{dx^n} + \frac{\kappa(\kappa-1)}{1.2} u^2 \frac{d^n u^{\kappa-2}}{dx^n} + \ldots$$

$$+ (-1)^{\kappa-1} \kappa u^{\kappa-1} \frac{d^n u}{dx^n} (\kappa = 1, 2, \ldots, n).$$

[First notice that the nth derivative may be written in the form (a), where the coefficients $A_1, A_2, \ldots, A_n$ are independent of the form of the function $\phi(u)$. To find their values, set $\phi(u)$ equal to $u, u^2, \ldots, u^n$ successively, and solve the resulting equations for $A_1, A_2, \ldots, A_n$. The result is the form (b)].

I have quoted the problem and the suggestions in full, and shall now proceed to give several proofs for it, in the hope that these proofs will illustrate certain operations with series which might be useful in similar work.

I. Let $y = \phi(u)$, wherein u is a function of x. Then

$$\frac{dy}{dx} = \frac{dy}{du} \cdot \frac{du}{dx} = \phi'(u) \frac{du}{dx}.$$

$$\frac{d^2 y}{dx^2} = \phi'(u) \frac{d^2 u}{dx^2} + \phi''(u) \left(\frac{du}{dx}\right)^2.$$

$$\frac{d^3 y}{dx^3} = \phi'(u) \frac{d^3 u}{dx^3} + 3\phi''(u) \frac{du}{dx} \frac{d^2 u}{dx^2} + \phi'''(u) \left(\frac{du}{dx}\right)^3.$$

We now assume
$$\frac{d^n y}{dx^n} = \frac{A_1}{1!}\phi'(u) + \frac{A_2}{2!}\phi''(u) + \frac{A_3}{3!}\phi'''(u) + \ldots + \frac{A_n}{n!}\phi^n(u), \quad (1)$$
wherein the A's are functions of u and x, but independent of $\phi(u)$.

To show that (1) is true, we must show that it holds also for the $n+1$st derivative.

Differentiating (1) with respect to x, we have

$$\frac{d^{n+1}y}{dx^{n+1}} = \phi'(u)\frac{d}{dx}\frac{A_1}{1!} + \phi''(u)\left[\frac{A_1}{1!}\frac{du}{dx} + \frac{d}{dx}\frac{A_2}{2!}\right]$$

$$+ \phi'''(u)\left[\frac{A_2}{2!}\frac{du}{dx} + \frac{d}{dx}\frac{A_3}{3!}\right] + \ldots \phi^{n-1}(u)\left[\frac{A_{n-2}}{(n-2)!}\frac{du}{dx} + \frac{d}{dx}\frac{A_{n-1}}{(n-1)!}\right]$$

$$+ \phi^n(u)\left[\frac{A_{n-1}}{(n-1)!}\frac{du}{dx} + \frac{d}{dx}\frac{A_n}{n!}\right] + \phi^{n+1}(u)\frac{A_n}{n!}\frac{du}{dx}$$

$$= \frac{B}{1!}\phi'(u) + \frac{B_2}{2!}\phi''(u) + \frac{B_3}{3!}\phi'''(u) + \ldots + \frac{B_n}{n!}\phi^n(u) + \frac{B_{n+1}}{(n+1)!}\phi^{n+1}(u),$$

which is of the same form as (1).

We shall now determine the coefficients represented by the A's in (1). Since the A's are independent of y, they will have the same value whatever $\phi(u)$ might be.

Letting therefore:

$y = u$, then $\dfrac{d^n u}{dx^n} = A_1$;

$y = u^2$, ,, $\dfrac{d^n u^2}{dx^n} = 2u A_1 + A_2$;

$y = u^3$, ,, $\dfrac{d^n u^3}{dx^n} = 3u^2 A_1 + 3u A_2 + A_3$;

. . . .

$y = u^\kappa$, ,, $\dfrac{d^n u^\kappa}{dx^n} = \binom{\kappa}{1}u^{\kappa-1}A_1 + \binom{\kappa}{2}u^{\kappa-2}A_2 + \ldots + \binom{\kappa}{\kappa-1}u A_{\kappa-1} + A_\kappa.$

Solving these equations for the A's, we obtain

$$A_1 = \frac{d^n u}{dx^n},$$

$$A_2 = \frac{d^n u^2}{dx^n} - \binom{2}{1}u\frac{d^n u}{dx^n},$$

$$A_3 = \frac{d^n u^3}{dx^n} - \binom{3}{1}u\frac{d^n u^2}{dx^n} + \binom{3}{2}u^2\frac{d^n u}{dx^n}.$$

Let us now assume

$$A_\kappa = \sum_{\lambda=0}^{\kappa} (-1)^\lambda \binom{\kappa}{\lambda} u^\lambda \frac{d^n}{dx^n} u^{\kappa-\lambda}. \quad . \quad . \quad . \quad (2)$$

Now if $y = u^{\kappa+1}$, then from (1) follows

$$\frac{d^n u^{\kappa+1}}{dx^n} = \binom{\kappa+1}{1} u^\kappa A_1 + \binom{\kappa+1}{2} u^{\kappa-1} A_2 + \ldots + \binom{\kappa+1}{\kappa} u A_\kappa + A_{\kappa+1}$$

and

$$A_{\kappa+1} = \frac{d^n u^{\kappa+1}}{dx^n} - \sum_{\lambda=1}^{\kappa} \binom{\kappa+1}{\lambda} u^{\kappa-\lambda+1} A_\lambda.$$

But

$$A_\lambda = \sum_{\gamma=0}^{\lambda} (-1)^\gamma \binom{\lambda}{\gamma} u^\gamma \frac{d^n u^{\lambda-\gamma}}{dx^n},$$

for values of λ from 1 to κ inclusive.
Therefore

$$A_{\kappa+1} = \frac{d^n u^{\kappa+1}}{dx^n} - \sum_{\lambda=1}^{\kappa} \sum_{\gamma=0}^{\lambda} (-1)^\gamma \binom{\kappa+1}{\lambda} \binom{\lambda}{\gamma} u^{\kappa+1-\lambda+\gamma} \frac{d^n u^{\lambda-\gamma}}{dx^n}.$$

Denoting the double summation by S and letting $\lambda = \kappa + 1 - \alpha$, and in turn $\alpha + \gamma = \beta$, we have

$$S = \sum_{\alpha=1}^{\kappa} \sum_{\beta=\alpha}^{\kappa+1} (-1)^{\beta-\alpha} \binom{\kappa+1}{\alpha} \binom{\kappa+1-\alpha}{\beta-\alpha} u^\beta \frac{d^n u^{\kappa+1-\beta}}{dx^n}$$

$$= \sum_{\alpha=1}^{\kappa} \sum_{\beta=\alpha}^{\kappa} (-1)^{\beta-\alpha} \binom{\kappa+1}{\alpha} \binom{\kappa+1-\alpha}{\beta-\alpha} u^\beta \frac{d^n u^{\kappa+1-\beta}}{dx^n}, \quad (3)$$

since for $\beta = \kappa + 1$, $\quad \dfrac{d^n u^{\kappa+1-\beta}}{dx^n} = 0$.

Now

$$\sum_{\alpha=1}^{\kappa} \sum_{\beta=\alpha}^{\kappa} M_{\alpha, \beta} = \sum_{\beta=1}^{\kappa} \sum_{\alpha=1}^{\beta} M_{\alpha, \beta}.$$

This can be shown in the following way:

$$\sum_{\alpha=1}^{\kappa} \sum_{\beta=\alpha}^{\kappa} M_{\alpha,\beta} = M_{1,1} + M_{1,2} + M_{1,3} + \ldots + M_{1,\kappa}$$
$$+ M_{2,2} + M_{2,3} + \ldots + M_{2,\kappa}$$
$$+ M_{3,3} + \ldots + M_{3,\kappa}$$
$$+ \ldots \ldots$$
$$+ M_{\kappa,\kappa}.$$

Adding by columns we have

$$\sum_{a=1}^{\kappa} \sum_{\beta=a}^{\kappa} M_{a,\beta} = M_{1,1} + (M_{1,2} + M_{2,2}) + \ldots + (M_{1,\kappa} + M_{2,\kappa} + \ldots + M_{\kappa,\kappa})$$

$$= \sum_{\beta=1}^{\kappa} \sum_{a=1}^{\beta} M_{a,\beta}.$$

By means of (4) the form (3) changes to

$$S = \sum_{\beta=1}^{\kappa} (-1)^{\beta} \sum_{a=1}^{\beta} (-1)^{a} \binom{\kappa+1}{\alpha} \binom{\kappa+1-\alpha}{\beta-\alpha} u^{\beta} \frac{d^n u^{\kappa+1-\beta}}{dx^n}$$

$$= \sum_{\beta=1}^{\kappa} (-1)^{\beta} u^{\beta} \frac{d^n u^{\kappa+1-\beta}}{dx^n} \sum_{a=1}^{\beta} (-1)^{a} \binom{\kappa+1}{\alpha} \binom{\kappa+1-\alpha}{\beta-\alpha}.$$

Now

$$\binom{\kappa+1}{\alpha} \binom{\kappa+1-\alpha}{\beta-\alpha} = \frac{(\kappa+1)!}{(\kappa+1-\alpha)!\,\alpha!} \cdot \frac{(\kappa+1-\alpha)!}{(\kappa+1-\beta)!\,(\beta-\alpha)!} \cdot \frac{\beta!}{\beta!}$$

$$= \frac{(\kappa+1)!}{(\kappa+1-\beta)!\,\beta!} \cdot \frac{\beta!}{(\beta-\alpha)!\,\alpha!} = \binom{\kappa+1}{\beta}\binom{\beta}{\alpha}.$$

Therefore

$$S = \sum_{\beta=1}^{\kappa} (-1)^{\beta} \binom{\kappa+1}{\beta} u^{\beta} \frac{d^n u^{\kappa+1-\beta}}{dx^n} \sum_{a=1}^{\beta} (-1)^{a} \binom{\beta}{\alpha}.$$

But $\displaystyle \sum_{a=1}^{\beta} (-1)^{a} \binom{\beta}{\alpha} = \sum_{a=0}^{\beta} (-1)^{a} \binom{\beta}{\alpha} - 1 = (1-1)^{\beta} - 1 = -1,$

and (5) becomes

$$S = \sum_{\beta=1}^{\kappa} (-1)^{\beta} \binom{\kappa+1}{\beta} u^{\beta} \frac{d^n u^{\kappa+1-\beta}}{dx^n}.$$

Hence

$$A_{\kappa+1} = \frac{d^n u^{\kappa+1}}{dx^n} + \sum_{\beta=1}^{\kappa} (-1)^{\beta} \binom{\kappa+1}{\beta} u^{\beta} \frac{d^n u^{\kappa+1-\beta}}{dx^n}$$

$$= \sum_{\beta=0}^{\kappa} (-1)^{\beta} \binom{\kappa+1}{\beta} u^{\beta} \frac{d^n u^{\kappa+1-\beta}}{dx^n}, \text{ since } \frac{d^n u^{\kappa+1-\kappa-1}}{dx^n} = 0,$$

and $A_{\kappa+1}$ is of the same form as the one assumed for A_{κ} in (2).

II. The following is another method for proving the given theorem.

Let κ successive operations $u\dfrac{d}{du}$ each on $\phi(u)$, that is

$$\left[\left(u\frac{d}{du}\right)\left(u\frac{d}{du}\right)\left(u\frac{d}{du}\right)\ldots\ldots\kappa \text{ operations}\right]\phi(u)$$

wherein u and $\dfrac{d}{du}$ are not permutable, be designated by

$$\left(u\frac{d}{du}\right)^{\kappa}\phi(u),$$

then

$$\left(u\frac{d}{du}\right)^{\kappa}\phi(u)=\overset{n}{\underset{\kappa=1}{\Sigma}}\frac{1}{\kappa!}\overset{\kappa-1}{\underset{a=0}{\Sigma}}(-1)^{a}\binom{\kappa}{\alpha}(\kappa-\alpha)^{n}\,u^{\kappa}\frac{d^{\kappa}\phi(u)}{du^{\kappa}}.$$

Let $\quad u=e^{x}$, then $\left(u\dfrac{d}{du}\right)^{n}=\left(u\dfrac{\dfrac{d}{dx}}{\dfrac{du}{dx}}\right)^{n}=\left(\dfrac{d}{dx}\right)^{n}$,

therefore

$$\frac{d^{n}\phi(u)}{dx^{n}}=\overset{n}{\underset{\kappa=1}{\Sigma}}\frac{1}{\kappa!}\overset{\kappa-1}{\underset{a=0}{\Sigma}}(-1)^{a}\binom{\kappa}{\alpha}(\kappa-\alpha)^{n}\,e^{\kappa x}\phi^{(\kappa)}(e^{x}).$$

But $\qquad (\kappa-\alpha)^{n}\,e^{\kappa x}=e^{\alpha x}(\kappa-\alpha)^{n}\,e^{(\kappa-\alpha)x}$

$$=e^{a\kappa}\frac{d^{n}\,e^{(\kappa-a)x}}{da^{n}}$$

$$=u\frac{d^{n}u^{\kappa-a}}{dx^{n}}.$$

Hence

$$\frac{d^{n}\phi(u)}{dx^{n}}=\overset{n}{\underset{\kappa=1}{\Sigma}}\frac{1}{\kappa!}\overset{\kappa-1}{\underset{a=0}{\Sigma}}(-1)^{a}\binom{\kappa}{\alpha}u^{a}\frac{d^{n}}{dx^{n}}u^{\kappa-a}\,\phi^{(\kappa)}(u).$$

III. A third way of proving the theorem is as follows :—

$$\frac{dy}{dx}=\frac{dy}{du}\cdot\frac{du}{dx},$$

$$\frac{d^{2}y}{dx^{2}}=\frac{d^{2}u}{dx^{2}}\cdot\frac{dy}{du}+\left(\frac{du}{dx}\right)^{2}\frac{d^{2}y}{du^{2}},$$

but $\qquad\left(\dfrac{du}{dx}\right)^{2}=\dfrac{1}{2!}\left[\dfrac{d^{2}u^{2}}{dx^{2}}-\binom{2}{1}u\dfrac{d^{2}u}{dx^{2}}\right],$

therefore $\qquad\dfrac{d^{2}y}{dx^{2}}=\overset{2}{\underset{\kappa=1}{\Sigma}}\dfrac{1}{\kappa!}\overset{\kappa-1}{\underset{a=0}{\Sigma}}(-1)^{a}\binom{\kappa}{\alpha}u^{a}\dfrac{d^{2}u^{\kappa-a}}{dx^{2}}\dfrac{d^{\kappa}y}{du^{\kappa}}.\quad\cdot\;(1)$

Again $\quad \dfrac{d^3y}{dx^3} = \dfrac{d^3u}{dx^3}\dfrac{dy}{du} + 3\dfrac{d^2u}{dx^2}\cdot\dfrac{du}{dx}\dfrac{d^2y}{du^2} + \left(\dfrac{du}{ax}\right)^3\dfrac{d^3y}{du^3}.$

Since $\quad\quad \dfrac{d^3u^2}{dx^3} = 6\dfrac{d^2u}{dx^2}\dfrac{du}{dx} + 2u\dfrac{d^3u}{dx^3},$

and $\quad\quad\quad \dfrac{d^3u^3}{dx^3} = 3u^2\dfrac{d^3u}{dx^3} + 18u\dfrac{du}{dx}\dfrac{d^2u}{dx^2} + 6\left(\dfrac{du}{dx}\right)^3,$

therefore $\quad 3\dfrac{d^2u}{dx^2}\cdot\dfrac{du}{dx} = \dfrac{1}{2!}\left[\dfrac{d^3u^2}{dx^3} - \binom{2}{1}u\dfrac{d^3u}{dx^3}\right],$

and $\quad\quad \left(\dfrac{du}{dx}\right)^3 = \dfrac{1}{3!}\left[\dfrac{d^3u^3}{dx^3} - \binom{3}{1}u\dfrac{d^3u^2}{dx^3} + \binom{3}{2}u^2\dfrac{d^3u}{dx^3}\right],$

and hence

$$\dfrac{d^3y}{dx^3} = \dfrac{d^3u}{dx^3}\dfrac{dy}{du} + \dfrac{1}{2!}\left[\dfrac{d^3u^2}{dx^3} - \binom{2}{1}u\dfrac{d^3u}{dx^3}\right]\dfrac{d^2y}{du^2}$$

$$+ \dfrac{1}{3!}\left[\dfrac{d^3u^3}{dx^3} - \binom{3}{1}u\dfrac{d^3u^2}{dx^3} + \binom{3}{2}u^2\dfrac{d^3u}{dx^3}\right]\dfrac{d^3y}{du^3},$$

or written symbolically

$$\dfrac{d^3y}{dx^3} = \sum_{\kappa=1}^{3}\dfrac{1}{\kappa!}\sum_{\alpha=0}^{\kappa-1}(-1)^\alpha\binom{\kappa}{\alpha}u^a\dfrac{d^3u^{\kappa-a}}{dx^3}\dfrac{d^\kappa y}{du^\kappa}. \quad . \quad (2)$$

Let us assume that this form holds for all values of n from 1 to n inclusive, that is

$$\dfrac{d^n y}{dx^n} = \sum_{\kappa=1}^{n}\dfrac{1}{\kappa!}\sum_{\alpha=0}^{\kappa-1}(-1)^\alpha\binom{\kappa}{\alpha}u^a\dfrac{d^n u^{\kappa-a}}{dx^n}\dfrac{d^\kappa y}{du^\kappa}\cdot\cdot \quad . \quad (3)$$

We shall then prove that this form holds also for $\dfrac{d^{n+1}y}{dx^{n+1}}$.

Differentiating (3) gives

$$\dfrac{d^{n+1}y}{dx^{n+1}} = \sum_{\kappa=1}^{n}\dfrac{1}{\kappa!}\sum_{\alpha=0}^{\kappa-1}(-1)^\alpha\binom{\kappa}{\alpha}u^a\dfrac{d^n u^{\kappa-a}}{dx^n}\dfrac{d^{\kappa+1}y}{du^{\kappa+1}}\dfrac{du}{dx}$$

$$+ \sum_{\kappa=1}^{n}\dfrac{1}{\kappa!}\sum_{\alpha=0}^{\kappa-1}(-1)^\alpha\binom{\kappa}{\alpha}\dfrac{d}{dx}\left\{u^a\dfrac{d^n u^{\kappa-a}}{dx^n}\right\}.$$

Now $\quad\quad \sum_{\kappa=1}^{n}\left[\sum_{\alpha=0}^{\kappa-1}(-1)^\alpha\binom{\kappa}{\alpha}\dfrac{d}{dx}\left\{u^a\dfrac{d^n u^{\kappa-a}}{dx^n}\right\}\right]$

$$= \sum_{\kappa=2}^{n}\sum_{\alpha=1}^{\kappa-1}(-1)^\alpha\alpha u^{a-1}\dfrac{du}{dx}\dfrac{d^n u^{\kappa-a}}{dx^n} + \sum_{\kappa=1}^{n}\sum_{\alpha=0}^{\kappa-1}(-1)^\alpha\binom{\kappa}{\alpha}u^a\dfrac{d^{n+1}u^{\kappa-a}}{dx^{n+1}}.$$

Therefore

$$\frac{d^{n+1}y}{dx^{n+1}} = \sum_{\kappa=2}^{n+1}\left[\sum_{a=0}^{\kappa-1}(-1)^a\binom{\kappa-1}{\alpha}u^\alpha\frac{d^n u^{\kappa-a-1}}{dx^n}\right]\frac{1}{(\kappa-1)!}\frac{du}{dx}\cdot\frac{d^\kappa y}{du^\kappa}$$

$$-\sum_{\kappa=2}^{n}\left[\sum_{a=0}^{\kappa-2}(-1)^a\binom{\kappa}{\alpha+1}(\alpha+1)u^\alpha\frac{d^n}{dx^n}u^{\kappa-a-1}\right]\frac{1}{\kappa!}\frac{du}{dx}\frac{d^\kappa y}{dx^\kappa}$$

$$+\sum_{\kappa=1}^{n}\left[\sum_{a=0}^{\kappa-1}(-1)^a\binom{\kappa}{\alpha}u^a\frac{d^{n+1}}{dx^{n+1}}u^{\kappa-a}\right]\frac{1}{\kappa!}\frac{d^\kappa y}{dx^\kappa}\cdot \quad . \quad . \quad . \quad (4)$$

But

$$\binom{\kappa}{\alpha+1}\frac{\alpha+1}{\kappa!}=\binom{\kappa-1}{\alpha}\frac{1}{(\kappa-1)!},$$

therefore

$$\frac{d^{n+1}y}{dx^{n+1}}\left[\sum_{a=0}^{n-1}(-1)^a\binom{n}{\alpha}u^a\frac{d^n u^{n-a}}{dx^n}\right]\frac{1}{n!}\frac{du}{dx}\frac{d^{n+1}y}{du^{n+1}}$$

$$+\sum_{\kappa=1}^{n}\frac{1}{\kappa!}\sum_{a=0}^{\kappa-1}(-1)^a\binom{\kappa}{\alpha}u^a\frac{d^{n+1}u^{\kappa-a}}{dx^{n+1}}\frac{d^\kappa y}{du^\kappa}. \quad . \quad . \quad (5)$$

We must now show that

$$\frac{1}{n!}\frac{du}{dx}\frac{d^{n+1}y}{du^{n+1}}\left[\sum_{a=0}^{n-1}(-1)^a\binom{n}{\alpha}u^a\frac{d^n u^{n-a}}{dx^n}\right]$$

$$=\frac{1}{n+1}\frac{d^{n+1}}{dx^{n+1}}\left[\sum_{a=0}^{n}(-1)^a\binom{n+1}{\alpha}u^a\frac{d^{n+1}u^{n+1-a}}{dx^{n+1}}\right].$$

i. e.

$$(n+1)\sum_{\alpha=0}^{n+1}(-1)^a\binom{n}{\alpha}u^a\frac{d^n u^{n-a}}{dx^n}\frac{du}{dx}=\sum_{\alpha=0}^{n}(-1)^a\binom{n+1}{\alpha}u^a\frac{d^{n+1}u^{n+1-a}}{dx^{n+1}},$$

or if we let $n-\alpha=\beta$, we must show that

$$(n+1)\sum_{\beta=1}^{n}(-1)^\beta\binom{n}{\beta}u^{n-\beta}\frac{du}{dx}\frac{d^n u^\beta}{dx^n}=\sum_{\beta=0}^{n}(-1)^\beta\binom{n+1}{\beta+1}u^{n-\beta}\frac{d^{n+1}u^{\beta+1}}{dx^{n+1}}.$$

$$. \quad . \quad . \quad (6)$$

Now

$$\frac{d^{n+1}u^{\beta+1}}{dx^{n+1}}=(\beta+1)\frac{d^n}{dx^n}\left(u\frac{du}{dx}\right),$$

and (6) reduces to

$$\sum_{\beta=1}^{n}(-1)^\beta\binom{n}{\beta}u^{n-\beta}\frac{du}{dx}\frac{d^n u^\beta}{dx^n}=\sum_{\beta=0}^{n}(-1)^\beta\binom{n}{\beta}u^{n-\beta}\frac{d^n\left(u^\beta\frac{du}{dx}\right)}{dx^n}.$$

By Leibnitz's theorem for the derivative of a product we have

$$\sum_{\beta=0}^{n} (-1)^{\beta} \binom{n}{\beta} u^{n-\beta} \sum_{\gamma=1}^{n} \binom{n}{\gamma} \frac{d^{n-\gamma}}{dx^{n-\gamma}} u^{\beta} \frac{d^{\gamma+1}u}{dx^{\gamma+1}} = 0. \quad . \quad (7)$$

In order to prove (7), it is only necessary to show that it holds for $u = x^p$, when it becomes

$$x^{pn-n+p-1}\left[\sum_{\beta=0}^{n} \sum_{\gamma=1}^{n} (-1)^{\beta} \frac{(p\beta)!}{\beta!\,\gamma!\,(n-\beta)!\,(n-\gamma)!\,(p\beta-n+\gamma)!\,(p-\gamma+1)!}\right] = 0,$$

which is evidently independent of x. But when x is a constant, n is also a constant, and therefore (7) holds for all values of u. So that:

$$(n+1)\sum_{a=0}^{n-1} (-1)^a \binom{n}{a} u^a \frac{du}{dx} \frac{d^n u^{n-a}}{dx^n} = \sum_{a=0}^{n} (-1)^a \binom{n+1}{a} u^a \frac{d^{n+1}}{dx^{n+1}} u^{n+1-a},$$

and therefore

$$\frac{d^{n+1}y}{dx^{n+1}} = \sum_{\kappa=1}^{n+1} \frac{1}{\kappa!} \sum_{a=0}^{\kappa-1} (-1)^a \binom{\kappa}{a} u^a \frac{d^{n+1}u^{\kappa-a}}{dx^{n+1}} \frac{d^{\kappa}y}{du^{\kappa}}.$$

The following examples will illustrate the theorem.

To calculate

$$\text{(i.)} \quad \frac{d^{\kappa}}{dx^{\kappa}} \frac{x^m}{(1-x^n)^p}.$$

By Leibnitz's theorem for the derivative of a product of two functions,

$$\frac{d^{\kappa}}{dx^{\kappa}} \frac{x^m}{(1-x^n)^p} = \sum_{a=0}^{\kappa} \binom{\kappa}{a} \frac{d^{\kappa-a}}{dx^{\kappa-a}} x^m \frac{d^a}{dx^a} (1-x^n)^{-p}$$

$$= \kappa! \sum_{a=0}^{\kappa} \binom{m}{\kappa-a} \frac{x^{m-\kappa+a}}{a!} \frac{d^a}{dx^a} (1-x^n)^{-p}$$

$$= \kappa! \left[\binom{m}{\kappa} \frac{x^{m-\kappa}}{(1-x^n)^p} + \sum_{a=1}^{\kappa} \binom{m}{\kappa-a} \frac{x^{m-\kappa+a}}{a!} \frac{d^a}{dx^a} (1-x^n)^{-p}\right].$$

Let $x^n = u$, and $(1-u)^{-p} = y$, then

$$\frac{d^a y}{dx^a} = \sum_{\beta=1}^{a} \frac{1}{\beta!} \sum_{\gamma=0}^{\beta-1} (-1)^{\gamma} \binom{\beta}{\gamma} x^{n\gamma} \frac{d^a}{dx^a} x^{n(\beta-\gamma)} \frac{p(p+1)(p+2)\,..(p+\beta-1)}{(1-x^n)^{p+\beta}}$$

$$= \sum_{\beta=1}^{a} \frac{1}{\beta!} \sum_{\gamma=0}^{\beta-1} (-1)^{\gamma} \binom{\beta}{\gamma} \frac{(n\overline{\beta-\gamma})!}{(n\beta-\gamma-a)!} \frac{(p+\beta-1)!}{(p-1)!} \frac{x^{n\beta-a}}{(1-x^n)^{p+\beta}}.$$

Therefore

$$\frac{d^\kappa}{dx^\kappa}\frac{x^m}{(1-x^n)^p} = \kappa!\left[\binom{m}{\kappa}\frac{x^{m-\kappa}}{(1-x^n)^p} + \sum_{a=1}^{\kappa}\binom{m}{\kappa-a}x^{m-\kappa+a}\right.$$

$$\left.\times \sum_{\beta=1}^{a}\sum_{\gamma=0}^{\beta-1}(-1)^\gamma\binom{\beta}{\gamma}\binom{n\overline{\beta-\gamma}}{a}\binom{p+\beta-1}{\beta}\frac{x^{n\beta-a}}{(1-x^m)^{p+\beta}}\right]$$

$$= \kappa!\frac{x^{m-\kappa}}{(1-x^n)^p}\left[\binom{m}{\kappa}+\sum_{a=1}^{\kappa}\binom{m}{\kappa-a}\right.$$

$$\left.\times \sum_{\beta=1}^{a}\binom{p+\beta-1}{\beta}\frac{x^{m\beta}}{(1-x^n)^\beta}\sum_{\gamma=0}^{\beta-1}(-1)^\gamma\binom{\beta}{\gamma}\binom{n\overline{\beta-\gamma}}{a}\right].$$

(ii.) $\quad \dfrac{d^n}{dx^n}\dfrac{1}{(1-x^3+x^7)^p}.\quad$ Let $x^3-x^7=u$ and $(1-u)^{-p}=y$,

then

$$\frac{d^n y}{dx^n} = \sum_{\kappa=1}^{n}\frac{1}{\kappa!}\sum_{a=0}^{\kappa-1}(-1)^a\binom{\kappa}{a}u^a\frac{d^n}{dx^n}u^{\kappa-a}\frac{d^\kappa y}{du^\kappa}.$$

Now

$$\frac{d^\kappa y}{du^\kappa} = \frac{d^\kappa}{du^\kappa}(1-u)^{-p} = \kappa!\binom{p+\kappa-1}{\kappa}(1-u)^{-(p+\kappa)},$$

and

$$\frac{d^n}{dx^n}u^{\kappa-a} = \frac{d^n}{dx^n}(x^3-x^7)^{\kappa-a} = \frac{d^n}{dx^n}[x^3(1-x^4)]^{\kappa-a}$$

$$= \frac{d^n}{dx^n}x^{3(\kappa-a)}\sum_{\beta=0}^{\kappa-a}(-1)^\beta\binom{\kappa-a}{\beta}x^{4\beta}$$

$$= n!\sum_{\beta=0}^{\kappa-a}(-1)^\beta\binom{\kappa-a}{\beta}\binom{3\kappa-3a+4\beta}{n}x^{3\kappa-3a+4\beta-n}.$$

Therefore

$$\frac{d^n y}{dx^n} = n!\sum_{\kappa=1}^{n}\frac{1}{\kappa!}\sum_{a=0}^{\kappa-1}(-1)^a\binom{\kappa}{a}(x^3-x^7)^a$$

$$\times\sum_{\beta=0}^{\kappa-a}(-1)^\beta\binom{\kappa-a}{\beta}\binom{3\kappa-3a+4\beta}{n}x^{3\kappa-3a+4\beta-n}\kappa!\binom{p+\kappa-1}{\kappa}(1-x^3+x^7)^{p-\kappa}$$

$$= \frac{n!}{x^n(1-x^3+x^7)^p}\sum_{\kappa=1}^{n}\sum_{a=0}^{\kappa-1}\binom{\kappa}{a}\sum_{\beta=0}^{\kappa-a}(-1)^{a+\beta}\binom{\kappa-a}{\beta}$$

$$\times\binom{3\kappa-3a+4\beta}{n}\binom{p+\kappa-1}{\kappa}\frac{(x^3-x^7)^a x^{3\kappa-3a+4\beta}}{(1-x^3+x^7)^\kappa}$$

$$= \frac{n!}{x^n(1-x^3+x^7)^p}\sum_{\kappa=1}^{n}\sum_{a=0}^{\kappa-1}\sum_{\beta=0}^{\kappa-a}(-1)^{a+\beta}\binom{\kappa}{a}\binom{\kappa-a}{\beta}$$

$$\times\binom{3\kappa-3a-4\beta}{n}\binom{p+\kappa-1}{\kappa}\frac{(1-x^4)^a x^{3\kappa+4\beta}}{(1-x^3+x^7)^\kappa}.$$

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LXXXVI. *On Self-Intersecting Lines of Force and Equi-potential Surfaces. By* G. B. JEFFERY, *M.A., B.Sc., Assistant in the Department of Applied Mathematics, University College, London* *.

BY a well-known theorem due to Rankine, if n sheets of an equipotential surface intersect at a point of equilibrium, they make equal angles π/n with each other. The object of this paper is to give some simple extensions of this theorem and some analogous results for lines of force. We will confine our attention to the cases in which the lines of force can be defined in terms of a force-function, *i. e.* when the field is either two-dimensional or has an axis of symmetry.

The case of a two-dimensional field admits of a very simple treatment. Both the potential ϕ and the force-function ψ satisfy the differential equation

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = 0. \quad \ldots \ldots \quad (1)$$

Taking the point of equilibrium in question as origin, the potential in its neighbourhood can be expressed in the form

$$\phi = H_n + H_{n+1} + H_{n+2} + \ldots, \quad \ldots \quad (2)$$

where H_n is a homogeneous function of the coordinates of degree n. Each term of this series must be a solution of (1), and hence, in polar coordinates,

$$H_n = A r^n \sin(n\theta - \alpha). \quad \ldots \ldots \quad (3)$$

The tangents to the branches of the equipotential surface at the origin are given by the roots of $H_n = 0$, *i. e.* by

$$\theta = \frac{\alpha}{n}, \quad \frac{\alpha+\pi}{n}, \quad \frac{\alpha+2\pi}{n}, \quad \ldots \ldots, \quad \frac{\alpha+(n-1)\pi}{n}.$$

Hence the n sheets of the equipotential surface make equal angles π/n with each other. It is obvious that in this case a precisely similar theorem holds for lines of force†. It remains to find the relation between the lines of force and the equipotential surfaces at the same point of equilibrium. ϕ and ψ are connected by the relations

$$\frac{\partial \phi}{\partial r} = \frac{1}{r}\frac{\partial \psi}{\partial \theta}, \quad \frac{1}{r}\frac{\partial \phi}{\partial \theta} = -\frac{\partial \psi}{\partial r},$$

* Communicated by the Author.

† A proof of this property for any curve defined by a solution of (1) was given by Stokes in a note appended to Rankine's paper, Proc. R. S. xv. 1867.

and from (3), by the aid of these relations,

$$\psi = A r^n \cos(n\theta - \alpha) + \textit{terms of higher degree in } r.$$

The directions of the lines of force are therefore given by

$$\theta = \frac{2\alpha + \pi}{2n}, \quad \frac{2\alpha + 3\pi}{2n}, \quad \cdots \cdots, \quad \frac{2\alpha + (2n-1)\pi}{2n}.$$

It appears that at a point where n equipotential lines intersect, n lines of force will also intersect. Further, these lines of force make equal angles π/n with each other and bisect the angles between the equipotential lines.

We pass on to the case of a three-dimensional field having an axis of symmetry. Let P be a point of equilibrium at a distance a from the axis of symmetry. Take the foot of the perpendicular from P to the axis of symmetry as the origin of cylindrical coordinates ϖ, z. ϕ and ψ no longer satisfy the same differential equation, but

$$\frac{\partial^2 \phi}{\partial \varpi^2} + \frac{1}{\varpi}\frac{\partial \phi}{\partial \varpi} + \frac{\partial^2 \phi}{\partial z^2} = 0, \quad \cdots \quad (4)$$

and

$$\frac{\partial^2 \psi}{\partial \varpi^2} - \frac{1}{\varpi}\frac{\partial \psi}{\partial \varpi} + \frac{\partial^2 \psi}{\partial z^2} = 0. \quad \cdots \quad (5)$$

Take polar coordinates through P in the meridian plane, the initial line being parallel to the axis of symmetry. Then

$$z = r \cos \theta, \qquad \varpi = a + r \sin \theta. \quad \cdots \quad (6)$$

Transforming (4) and (5) to the new coordinates, they become

$$(a + r \sin \theta)\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2}\right) \pm \left(\sin \theta \frac{\partial}{\partial r} + \cos \theta \frac{\partial}{r\partial \theta}\right) = 0, \quad (7)$$

where the upper sign is taken for the potential and the lower sign for the force-function.

In the neighbourhood of P let ϕ be expressed in the form

$$\phi = r^n \vartheta_n + r^{n+1}\vartheta_{n+1} + r^{n+2}\vartheta_{n+2} + \cdots,$$

where ϑ_n, ϑ_{n+1}, $\ldots\ldots$ are functions of θ only. Substituting in (7) the coefficients of the various powers of r in the expression so obtained must vanish separately. Equating the coefficient of r^{n-2} to zero, we have

$$\frac{d^2 \vartheta_n}{d\theta^2} + n^2 \vartheta_n = 0.$$

Hence, $\vartheta_n = A \sin(n\theta - \alpha)$

and

$$\phi = A r^n \sin(n\theta - \alpha) + \textit{terms in higher powers of } r. \quad . \quad (8)$$

The tangents in the meridian plane to the branches of the equipotential surface through P are in the directions

$$\theta = \frac{\alpha}{n}, \quad \frac{\alpha + \pi}{n}, \quad \ldots \ldots, \quad \frac{\alpha + (n-1)\pi}{n},$$

which agrees with Rankine's theorem.

ϕ and ψ are connected by the relations

$$\frac{\partial \phi}{\partial z} = \frac{1}{\varpi} \frac{\partial \psi}{\partial \varpi}, \quad \frac{\partial \phi}{\partial \varpi} = -\frac{1}{\varpi} \frac{\partial \psi}{\partial z},$$

which, by the aid of (6), transform into

$$\frac{\partial \phi}{\partial r} = \frac{1}{r(a + r \sin \theta)} \frac{\partial \psi}{\partial \theta}, \quad \frac{1}{r} \frac{\partial \phi}{\partial \theta} = -\frac{1}{a + r \sin \theta} \frac{\partial \psi}{\partial r}.$$

From these relations, together with (8), it is easy to obtain

$$\psi = -A a r^n \cos(n\theta - \alpha) + \textit{terms in higher powers of } r. \quad (9)$$

The tangents to the lines of force through P are therefore in the directions

$$\theta = \frac{2\alpha + \pi}{2n}, \quad \frac{2\alpha + 3\pi}{2n}, \quad \ldots \ldots, \quad \frac{2\alpha + (2n-1)\pi}{2n}.$$

Hence, at a point of equilibrium not lying on the axis of symmetry, the intersecting equipotential surfaces make equal angles with each other; the lines of force also make equal angles with each other, and bisect the angles between the equipotential surfaces.

If the point of equilibrium lies on the axis of symmetry, these results are no longer true. The potential in the neighbourhood of P can be expressed in terms of zonal harmonics,

$$\phi = A r^n P_n(\mu) + B r^{n+1} P_{n+1}(\mu) + \ldots, \quad . \quad . \quad (10)$$

where $\mu = \cos \theta$.

The tangents in the meridian plane to the equipotential surfaces through P are, therefore, given by the roots of $P_n(\mu) = 0$.

This equation has n distinct roots between $\mu = \pm 1$ exclusive.

Thus there are n sheets of the surface intersecting at P, but these do not make equal angles with each other. The axis of symmetry cannot be one of the equipotential lines, for $P_n(\mu)$ cannot vanish for $\theta = 0$ or π. When n is odd $\mu = 0$ is a root of $P_n(\mu) = 0$, and therefore when an odd number of sheets intersect one of them is normal to the axis of symmetry.

The force-function corresponding to (10) is well known to be *

$$\psi = \frac{A}{n+1} r^{n+1} (1 - \mu^2) \frac{d}{d\mu} P_n(\mu) + \text{higher powers of } r.$$

The lines of force through P are in the directions given by $\mu = \pm 1$, *i. e.* the two parts of the axis of symmetry, together with the roots of $\frac{d}{d\mu} P_n(\mu) = 0$. This equation has one and only one root between any two consecutive roots of

Fig. 1.
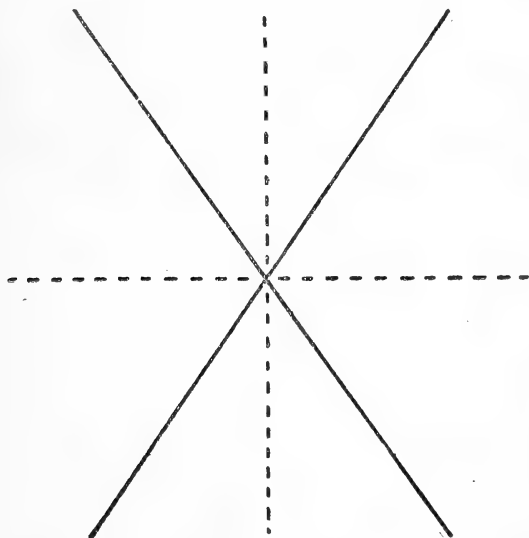
The Intersection of Two Lines of Force and Two Sheets of an Equipotential Surface.

$P_n(\mu) = 0$, and hence it has $n-1$ roots between $\mu = \pm 1$ exclusive. The axis of symmetry is, therefore, always one of the intersecting lines of force; there are $n-1$ others

* Lamb, 'Hydrodynamics,' p. 120.

making n lines of force which intersect at a point where n sheets of an equipotential surface intersect. These, again, will not make equal angles with each other, but one line of force will lie between every two consecutive sheets of the equipotential surface.

Fig. 2.
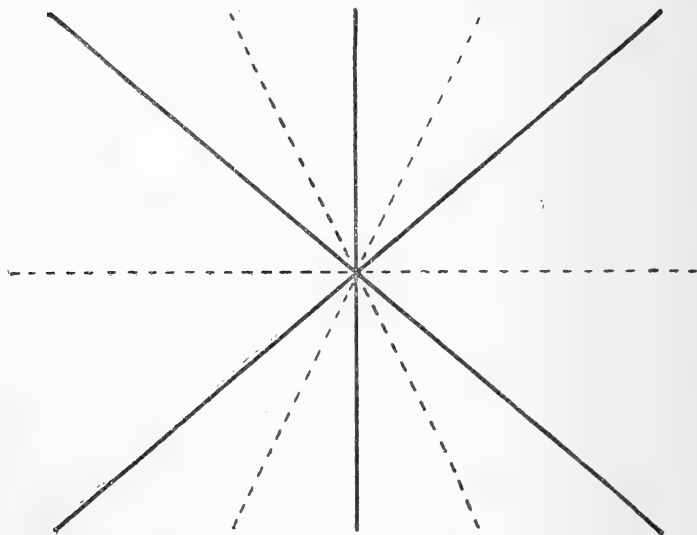
The Intersection of Three Lines of Force and Three Sheets of an Equipotential Surface.

The cases when two and three sheets intersect are shown in figs. 1 and 2. The firm lines represent the equipotentials and the broken lines the lines of force.

LXXXVII. *The Photographic Action of* α, β, *and* γ *Rays.*
By R. R. SAHNI, *M.A., Professor, Government College, Lahore* *.

[Plate XII.]

SEVERAL investigators have studied the action of α particles on sensitive films. Thus, Kinoshita† has shown that when such a film is exposed to an α-ray source, the photometric density of the film, on development, is proportional to the number of α particles incident on it; also that a single α particle produces a detectable effect on

the photographic plate. Reinganum * was the first to obtain tracks of single α particles in sensitive films; Michl † and, subsequently, Baisch ‡ and Mayer § also studied, in some detail, the photographic action of α particles. The tracks obtained by Reinganum and Michl were mostly curved, but, as Michl points out, this was probably due to the particular way in which the gelatine film contracts on drying. Walmsley and Makower ‖ were the first to publish a microphotograph of α-ray tracks. Some interesting microphotographs of α-ray tracks have been published in a recent paper by Kinoshita and Ikeuti ¶.

In the course of an investigation by the present writer, into certain properties of α and β rays, by the photographic method, it was found that most photographic plates, on development, show, under the microscope, a large number of blackened grains, even when they have not been previously exposed to light or some other stimulus, such as radiations from an active substance. It is clear that with a plate free from this defect, the examination of photographic films under the microscope should afford a very sensitive way of studying the properties of α rays, and the method would seem to be applicable to all the phenomena which have hitherto been investigated by the method of scintillations. The method has, in fact, been used by Mayer to study the scattering of α particles by metallic films. Both Reinganum and Mayer recommend the photomechanical and the Sigurd dia-positive plates, made by R. Jahr (Dresden), as being better than any other plates used by them ; but, as Mayer points out and as his results also show, even with these plates the number of grains visible under the microscope on an exposed plate was too large to permit the counting of α particles with accuracy.

In this short paper it is intended to describe a plate suitable for various kinds of investigations with the photographic method, and briefly to refer to some of the experiments which have been undertaken with it.

Selection of plate. — After considerable search with different kinds of plates, sensitive films, and papers with suitable developing solutions, it was found that Wratten and Wainwright's lantern-plate presented an absolutely clear surface. For a temperature of 18° C., which was

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* Reinganum, *Phys. Zeit.* xii. pp. 1076–77 (1911).
† Michl, *Akad. Wiss. Ber. Wien*, pp. 1431–1447 (1912).
‡ Baisch, *Ann. der Phys.* xxxv. p. 565 (1911).
§ Mayer, *Ann. der Phys.* xli. (1913).
‖ Walmsley & Makower, Proc. Phys. Soc. xxvi. (1914).
¶ Kinoshita & Ikeuti, Phil. Mag. March 1915.

considered to be the most convenient, a development of
about $2\frac{1}{2}$ minutes was the best. For lower temperatures,
this period was much longer. The other plates made by
the same firm gave unsatisfactory results. The Ilford
Process and the Imperial Sovereign plates come next after
the Wratten lantern-plates. The following developer was
found most suitable to be used with the plate :—

Solution A.

1. Quinol, 25 gm.
2. Potassium metabisulphite, 25 gm.
3. Potassium bromide, 25 gm.
4. Distilled water made up to 1000 c.c.

Solution B.

1. KOH, 50 gm.
2. Distilled water up to 1000 c.c.

Solutions A and B to be mixed in equal proportions
immediately before use.

A 20 per cent. solution of " Hypo " was used for fixing.

It is of importance to exclude even red light as much as
possible during all the operations. It is also important to
use water as free as possible from dust nuclei. For this
purpose the water for washing should be filtered or previously boiled and cooled.

Some experiments with α *particles.*—In the experiments
here referred to, both with α and β particles, the active
sources employed consisted of polonium (containing some
radium E), thorium active deposit, and radium C on the
tip of fine sewing-needles and on suitable metal plates of
different dimensions. In the case of the needles, only the
tip was effective, the rays from the rest of a needle, if activated, being screened off by means of a small cardboard disk.

The microphotograph in Plate XII. fig. 1 was obtained
with a very weak thorium active deposit needle, the tip
being exposed for a few seconds to the sensitive plate.
Only a portion of the microphotograph is here shown. The
centre is about the point marked C. Fig. 2 (*a, b,* and *c*) was
obtained with a fairly strong polonium needle. Fig. 3 is a
portion of a similar microphotograph obtained with a thorium
active deposit needle. In all these cases the activated tip
of the needle was held in contact with the photographic
plate. Similar results were obtained with other α-ray
sources. It will be noticed, at once, that a marked feature
of all α-ray photographs is the presence of straight tracks
radiating from a common centre, which is either the point

of contact of the active tip with the sensitive plate, or, when the needle is held at a short distance above the plate, a point immediately below it. When the period of exposure is a sensible interval, a dark circular nucleus is formed. A careful examination of the radiating tracks will show the presence of an occasional track which is bent as the result of scattering. The α particles appear to suffer only one encounter, no tracks with more than one bend being visible. The peripheral tracks appear to be longer than those nearer the centre, but this is simply an optical effect, the central tracks being foreshortened. Fig. 1 shows this clearly.

It may be mentioned that, as was to be expected, the tracks produced with thorium active deposit were longer than those obtained with polonium. The longest track with thorium active deposit measured $48 \cdot 15\, \mu$, while the average length of the ten longest seen near the periphery was $32 \cdot 4\, \mu$. The longest track observed consisted of only 15 silver grains, while another track which measured $42 \cdot 0\, \mu$ was made up of 24 silver grains. The average number of grains in the ten longest tracks observed was $16 \cdot 8$. In all the above cases, care was taken to make sure by an examination with an oil immersion lens that the tracks did not consist of two separate ones in continuation of one another. Michl gives the length of the longest track with 9 grains as $32\, \mu$. He obtained tracks with 13 grains, Baisch mentions bent tracks with 15 grains, while Kinoshita and Ikeuti observed with radium C tracks with as many as 16 grains.

The action of β particles.—In 1911 C. T. R. Wilson *, in his well-known condensation experiments, made the tracks of β particles through moist air visible. The trails in this case were indicated by droplets of water condensed on the path of the β particles, thus forming cloud-like streaks which were immediately photographed. No one, however, seems to have obtained a photographic impression of separate β particles or studied a β photograph. A comparison between the α and β photographs reveals certain points of interest and practical importance.

The three active sources used in the experiments with α particles were also employed with β particles, the α particles being, in all cases, sifted off by wrapping the sensitive plate in paper of suitable thickness. Figs. 4 and 5 are microphotographs with β rays, the first with a thorium active deposit needle, and the second with the radium E needle. In both cases, the plate was wrapped up in black paper, in which it is ordinarily packed, as well as in one

* C. T. R. Wilson, Proc. Roy. Soc. ser. A, lxxxv. (1911).

thickness of aluminium foil weighing 7·5 mgs. per cm.², the active point being held next to the foil. A still greater enlargement of the edge of a photograph has also been studied with camera lucida sketches, noting down carefully the grains which became visible at different depths of the film. The distribution of the grains is so irregular that it is difficult to say with certainty whether there are definite tracks due to individual β particles. But if such tracks are present, they are certainly not straight.

It will be noticed at once that the β-ray photographs are quite different in character from those obtained with α rays. The following points of distinction may be noted :—

1. The distinct radial character of the α photographs is altogether absent in the β photographs. Compare specially α photographs fig. 2 (*a, b,* and *c*) with β photograph fig. 5. They were produced with the same active needle, and the magnification is also about the same.

2. In a β-ray photograph no straight tracks are visible.

3. In the case of a β photograph there is no well-defined centre, the dark nucleus, when formed, being irregular and nebulous.

Photographs have been taken by interposing an increasing number of aluminium foils of known thickness between the active source and the sensitive plate, activated plates as well as needles being used. The general character of the β-ray photographs, as indicated above, is maintained in all cases, the only difference noticed being a decrease in the photo-metric density or of the number per unit area of separate silver grains. A platinum plate which had been exposed to radium emanation for a couple of hours a month previously showed clearly the emission of both α and β rays due to the growth of the long-period active deposit.

The method is also being used for studying the weak activity of potassium and rubidium. Preliminary experiments show that they give off β rays *. It may be possible to discover other substances of still weaker activity by sufficiently increasing the period of exposure. Experiments in this direction are proceeding.

It will thus be clear that the Wratten lantern-plate affords an easy method for determining the emission or otherwise of α and β particles from a given substance, as well as of studying the complex character of β rays.

The action of γ *rays.*—A sensitive plate was exposed to 64 mgs. of radium contained in a thick glass tube at a distance of 4 cm. In one case, the rays had to penetrate

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* Campbell & Wood, Proc. Camb. Phil. Soc. xiv. p. 15 (1907).

through a lead plate 4 cm. thick ; in another case, a lead plate, 3 mm. thick, was interposed ; in a third series of experiments, a varying number of aluminium foils covered the sensitive plate ; while in a fourth case, the sensitive plate was exposed directly to the rays. All the photographs thus obtained resemble a β-ray photograph. In cases 3 and 4 the grains are apparently equally crowded, in 2 they are less crowded, while in 1 they are much thinner. Fig. 6 represents a photograph obtained in the second experiment given above. As expected, the γ-ray photographs were found to be similar to the β-ray photographs of the same magnification, since it is known that all the effects of γ rays are due to secondary β rays, which they excite.

The experiments described in this paper were preliminary to the use of the photographic method for determining, with accuracy, the scattering of α particles by gases.

In conclusion, the writer wishes to express his indebtedness to Dr. W. Makower for suggesting this research, and to him and to Dr. N. Bohr for their continued kind interest and advice during the progress of the experiments described in this paper. He is grateful to the Governing Body of the School of Technology for kindly placing the excellent resources of that institution at his disposal, and to Mr. R. B. Fishenden personally for kind and constant advice throughout the photographic operations. He also wishes to acknowledge the kindness of Dr. Hickling, of the Geological Department of this University, who was good enough to allow him the use of his microphotographical apparatus.

The Physical Laboratory,
Victoria University, Manchester.
March 1915.

LXXXVIII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

January 6th, 1915.—Dr. A. Smith Woodward, F.R.S., President, in the Chair.

THE following communications were read :—

1. ' The Silurian Inlier of Usk (Monmouthshire).' By Charles Irving Gardiner, M.A., F.G.S.

The Usk inlier lies a few miles north of Newport (Mon.). Between the coalfields of South Wales and the Forest of Dean the Old Red Sandstone is bent into an anticline, the axis of which runs

very nearly north and south. This has been denuded away to the west of Usk, and Silurian beds have been exposed, the rocks seen being of Ludlow and Wenlock age.

In the southern part of the inlier the Silurian rocks are arranged in two anticlinal folds, the axes of which run nearly north and south and dip southwards. These folds are separated by a fault. The western one is named the Coed-y-paen Anticline, the eastern one the Llangibby Anticline. The Old Red Sandstone is believed to rest unconformably on the Ludlow Beds along much of the margin of the Coed-y-paen Anticline, and beneath the Ludlow Beds, which are about 1300 feet thick, come 35 to 40 feet of a Wenlock Limestone, which covers Wenlock Shales: of these latter some 850 feet are seen. It is impossible to separate the Ludlow Beds into an upper and a lower series, owing to the absence of the Aymestry Limestone. They are composed mainly of sandy shales and sandstones above, and of sandy shales with layers of calcareous nodules or of calcareous bands below.

Dayia navicula is a common fossil up to 240 feet from the top of the Ludlow Shales, and *Holopella gregaria* and *H. obsoleta* occur only in the uppermost beds.

At their base the Ludlow Beds seem to pass conformably down into the Wenlock Beds, and the Wenlock Limestone is probably not at the summit of the Wenlock Shales. The Wenlock Limestone occurs either in irregular layers separated by sandy shales, or in massive beds largely made up of crinoid fragments. Corals are rare in it.

The Wenlock Shales below the limestone are divisible into an upper portion, which consists of sandy shales and sandstones, and a lower portion composed of mudstones. The Coed-y-paen Anticline has been much affected by pressure, the hard Wenlock Limestone Bed has been fractured in no fewer than twelve places, and portions of it driven in on to the soft underlying shales.

In the northern part of the area there is much alluvium and drift; consequently, although no Wenlock Limestone is now to be seen beyond the Wenlock Shales, it is possible that the limestone may occur beneath the drift, as, when last exposed, the Wenlock Shales are seen dipping north-eastwards, and beyond the drift Ludlow Beds are observed near Clytha. The Llangibby Anticline extends as far north as Cwm Dowlais, and shows Ludlow Beds resting upon Wenlock Limestone, the anticline ending against an east-and-west fault. North of Cwm Dowlais nothing but Ludlow Beds are seen between the Coed-y-paen Anticline and the Old Red Sandstone, from both of which they are faulted.

An account of the Ludlow Beds along the western and eastern sides of the inlier is given, and a large amount of evidence with regard to the ages of the rocks at numerous exposures is produced in the form of lists of fossils.

The fossils have all been named by Dr. F. R. Cowper Reed, who contributes an appendix in which several new species and varieties are described in detail.

2. 'Some Observations on Cone-in-Cone Structure and their Relation to its Origin.' By Samuel Rennie Haselhurst, M.Sc., F.G.S.

In a brief review our state of knowledge is summarized, and the deductions of other investigators are analysed.

The author then outlines the phenomenon of megascopic pseudostromatism, and certain tectonic features which are always associated with cone-in-cone structure in areas where it is greatly developed. He points to the disadvantage accruing from many observers not having seen it *in situ* on a large scale, and shows how a simulation of horizontality in stratification masks what he takes to be the key to the diagnosis of this structure.

Two typical areas are described :—

(a) The St. Mary's Island–Tynemouth district of the D_5 Coal-Measures of Northumberland.
(b) The Hawsker–Robin Hood's Bay–Ravenscar district of the North Riding of Yorkshire.

The specimens collected in these areas are unique, and some dozen types from other areas, including Sandown, Portmadoc, Olney, Somerton, Lyme Regis, and Merivale Park are examined in detail with reference to :—

(a) Evidence furnished by distorted fossils.
(b) Chemical composition.
(c) Geometrical similarities.
(d) Microscopic structures.

The author critically examines the accepted hypothesis that cone-in-cone structure is something essentially due to crystallization.

He describes the results of some high-pressure mimetic experiments, aided by a Royal Society grant which he now gratefully acknowledges. These experiments were designed to produce this structure, and reveal what the author believes to be many new points on the origin of concretions and cone-in-cone in particular. The experiments are new, inasmuch as the media used, namely : brittle, semi-plastic, and plastic, are enclosed in tunics of varied design, and then subjected either to a high uniform hydrostatic pressure or to a direct thrust. The results are in many ways analogous to those of Ewing, Goodman, and Daubrée who, it is remarked, did not attempt to explain cone-in-cone structures.

The author concludes from the evidence :

(i) that cone-in-cone is not due to crystallization, but is a mechanically produced structure due to great and localized pressure ;
(ii) that it is closely allied to the phenomenon known as pressure solution;
(iii) that cone-in-cone structure is closely associated with other rock-structures which are mutually indicative the one of the other, and also of their mode of origin.

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END OF THE TWENTY-NINTH VOLUME.

Fig. 4.

FIG. 1.

FIG. 2.

FIG. 3.
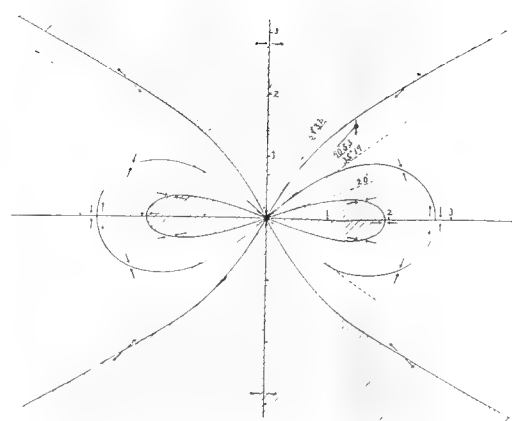
FIG. 4.
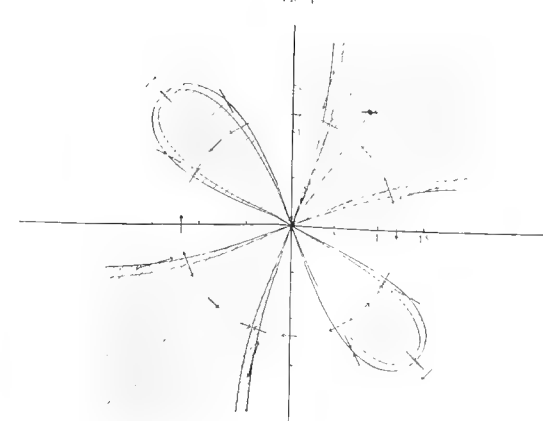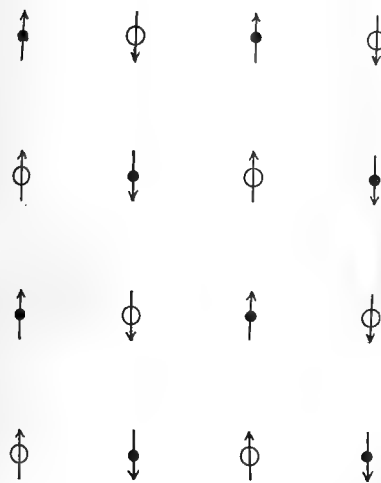
FIG. 5.

FIG. 6.
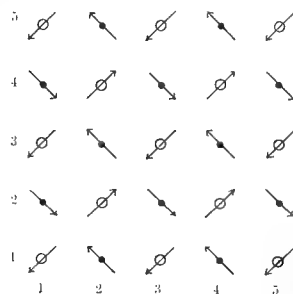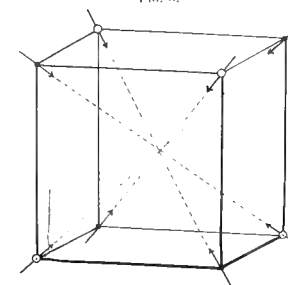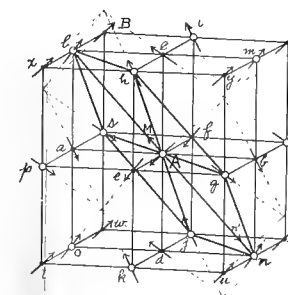
FIG. 7.

FIG. 8.

Odd planes horizontal.

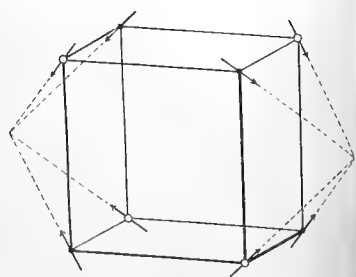Even planes horizontal.

FIG. 13.

FIG. 9.

FIG. 10.

FIG. 11.

FIG. 12.
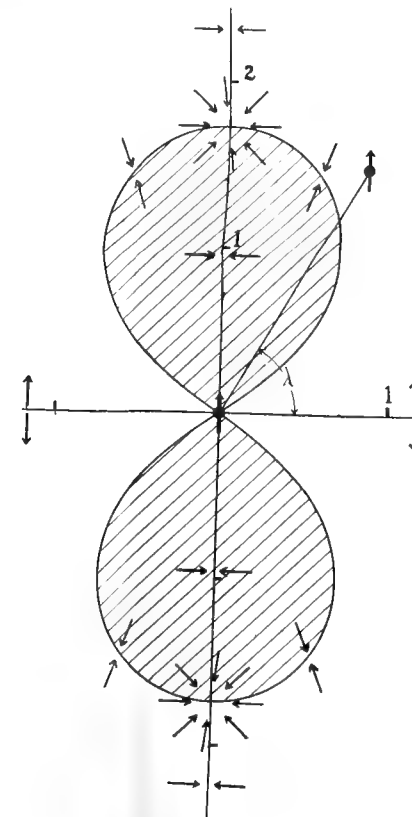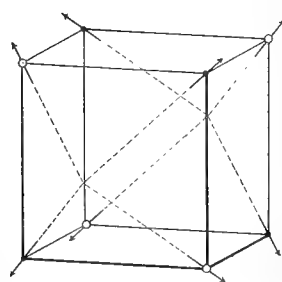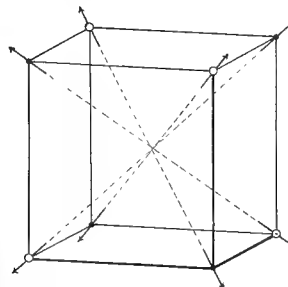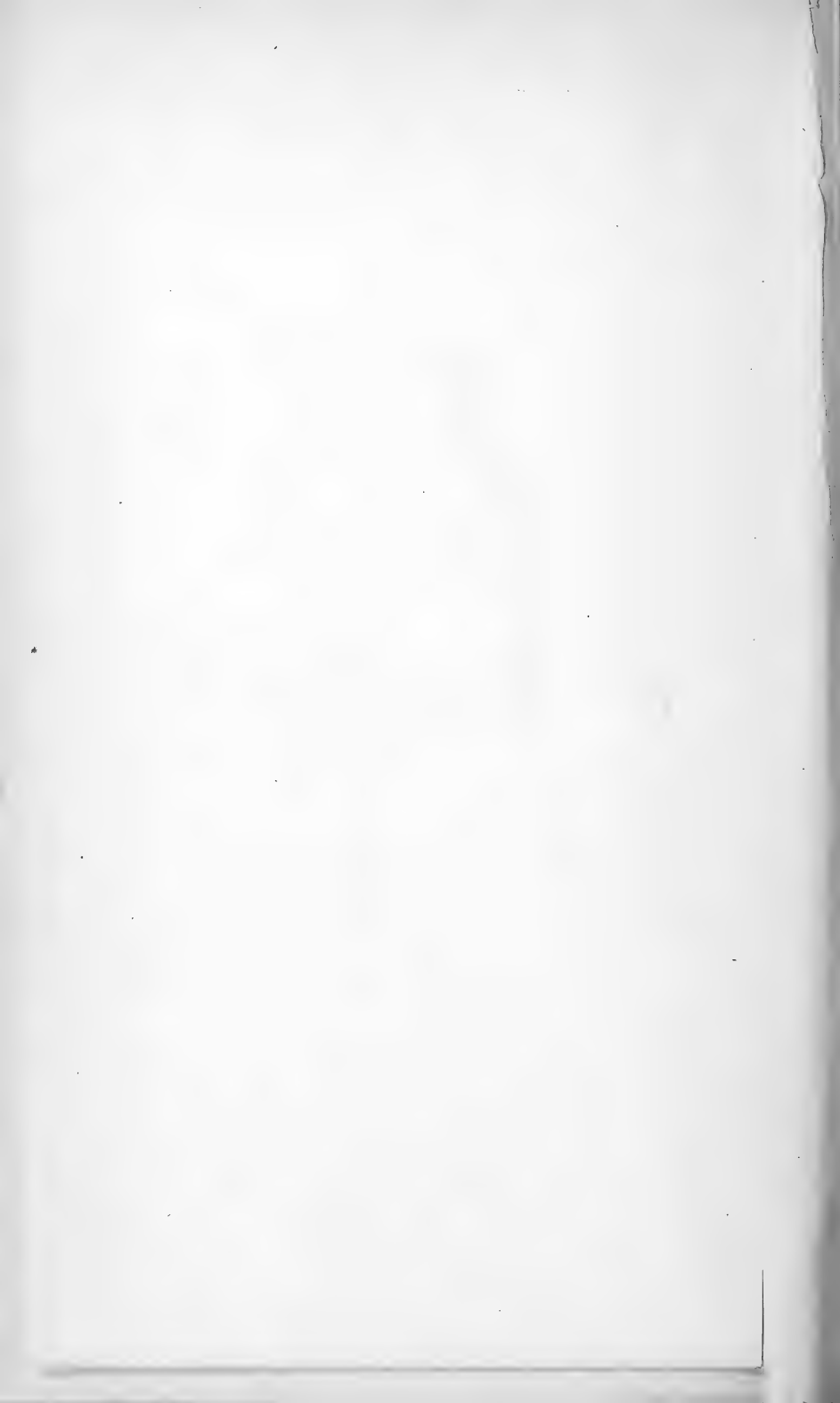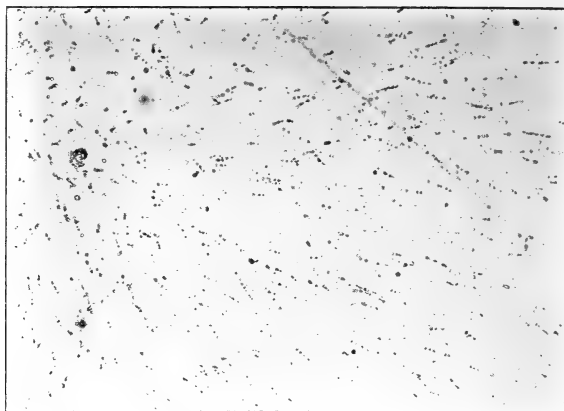
FIG. 1.—a rays from Th. Act. dep. ×210 diams.

a b c
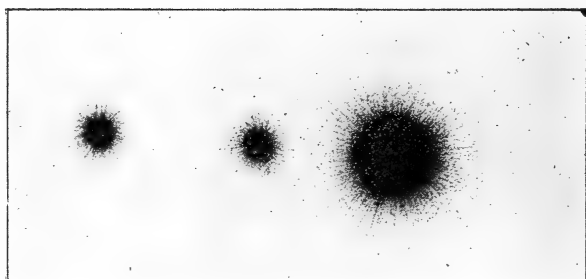
FIG. 2.—a rays from Polonium. ×55 diams.
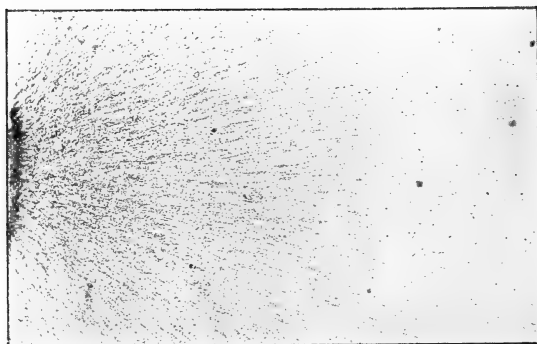
FIG. 3.—a rays from Th. Act. dep. ×65 diams.
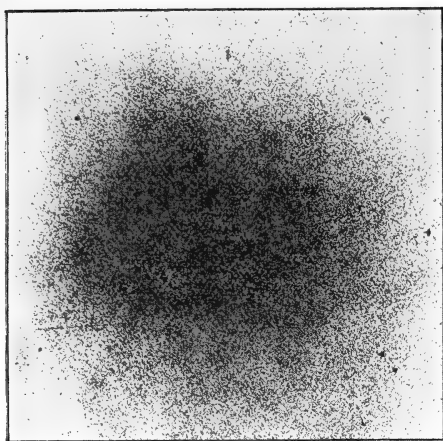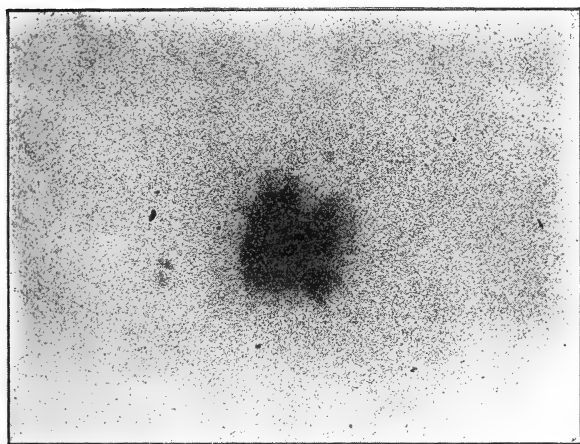
FIG. 4.—β rays from Th. Act. dep.   ×40 diams.
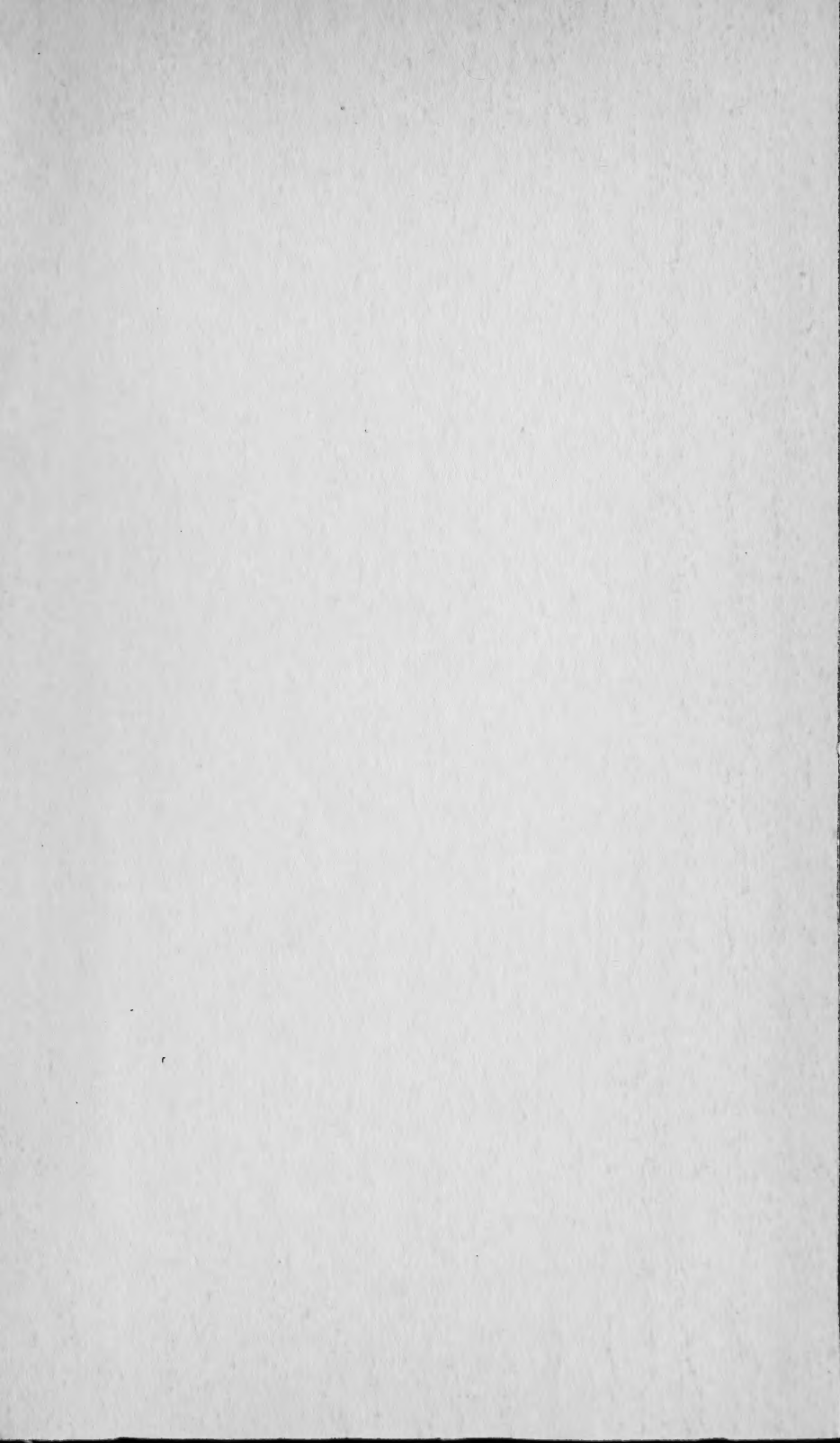

FIG. 5.—β rays from Radium E.   ×50 diams.
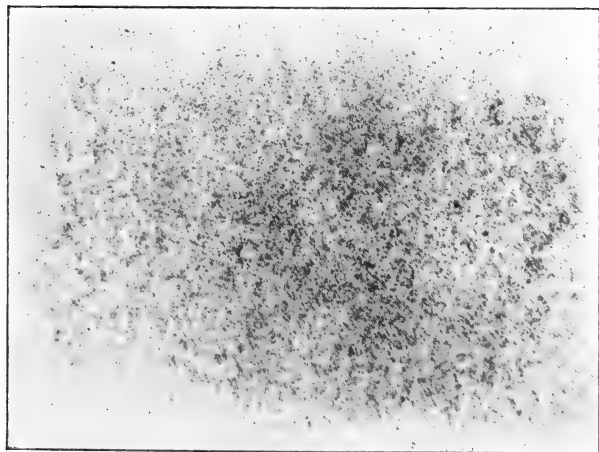
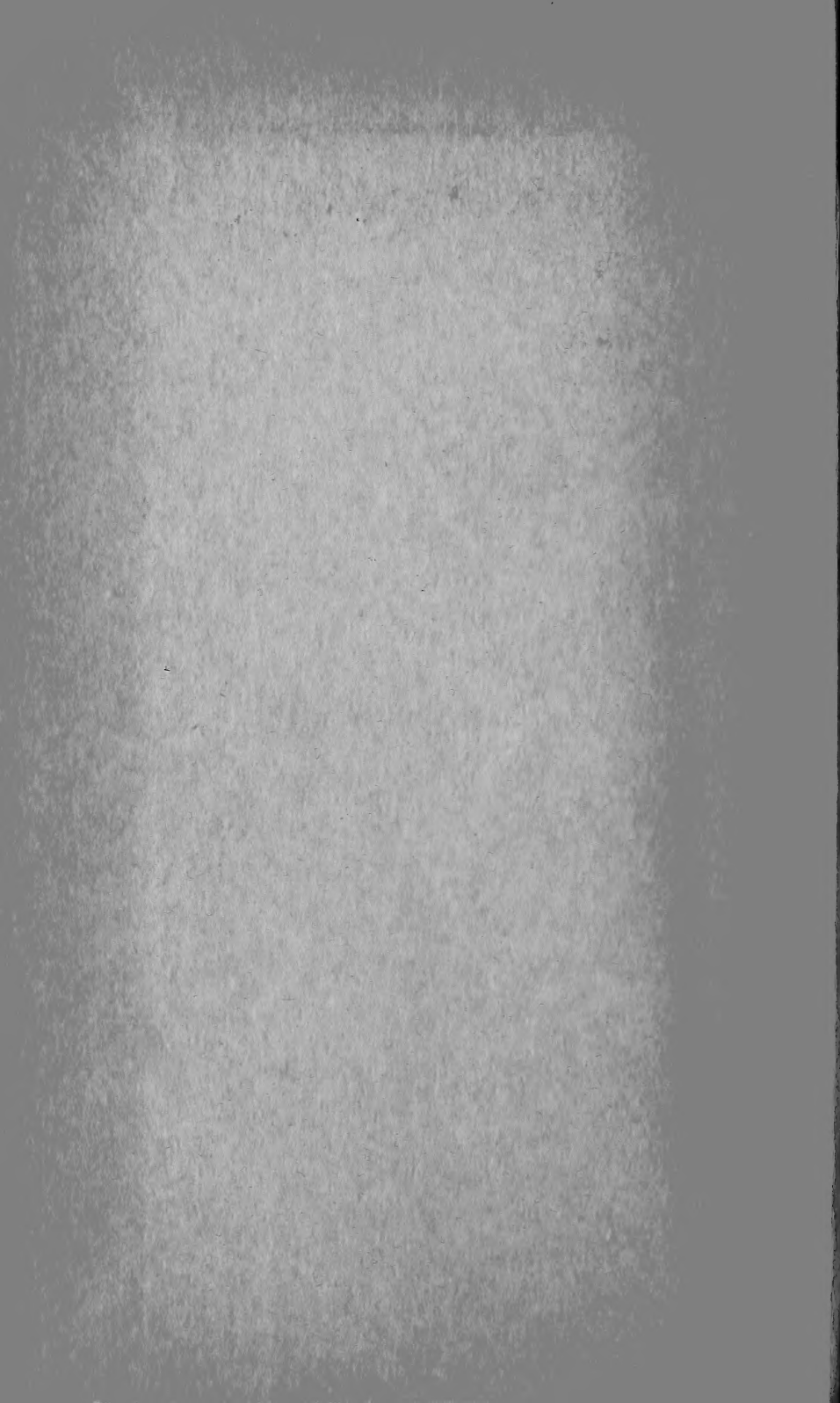FIG. 6.—γ rays from Radium.   ×260 diams.